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HAWAII AGRICULTURAL EXPERIMENT STATION,
J. M. WESTGATE, Agronomist in Charge.

Bulletin No. 41.

PHOSPHATE FERTILIZERS FOR HAWAIIAN SOILS, AND THEIR AVAILABILITY.

BY

WM. T. McGEORGE,
Former Chemist.

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HAWAII AGRICULTURAL EXPERIMENT STATION, HONOLULU.

[Under the supervision of A. C. TRUE, Director of the States Relations Service, United States Department of Agriculture.]

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LETTER OF TRANSMITTAL.

HONOLULU, HAWAII, *July 1, 1916.*

SIR: I have the honor to submit herewith, and recommend for publication as Bulletin No. 41 of the Hawaii Agricultural Experiment Station, a paper entitled "Phosphate Fertilizers for Hawaiian Soils, and Their Availability," by Wm. T. McGeorge, former chemist of the station. The use of phosphate fertilizer on Hawaiian soils is of extreme economic importance, owing to the unavailability of the large quantities naturally occurring in these soils. In the present paper several points of scientific and practical importance are brought out regarding (1) the influence of phosphate fertilizers on plant growth, (2) the availability of the naturally occurring phosphates, (3) the solubility of those phosphates as measured by various solvents, and (4) the chemical combinations in which phosphoric acid exists in Hawaiian soils. It appears that the primary factor in the nonavailability of phosphoric acid in Hawaiian soils is the peculiar physical condition of the soil and that phosphate fertilizers should be applied in a soluble form to produce the best results.

Respectfully,

J. M. WESTGATE,
Agronomist in Charge.

Dr. A. C. TRUE,
Director States Relations Service,
U. S. Department of Agriculture, Washington, D. C.

Recommended for publication.
A. C. TRUE, *Director.*

Publication authorized.
D. F. HOUSTON,
Secretary of Agriculture.

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PHOSPHATE FERTILIZERS FOR HAWAIIAN SOILS, AND THEIR AVAILABILITY.

INTRODUCTION.

It has been shown in previous publications of this station[1] that the local soils are rich in phosphoric acid, but that it is securely locked up in insoluble and unavailable combinations with the highly basic (and probably also with the silicic) soil constituents. Iron and aluminum, which occur in abundance, and lime, which occurs in widely varying amounts, are known to be active in this fixation, and it is highly probable that titanium, which occurs in large amounts in Hawaiian soils, is also an important factor in the fixation. In view of these peculiarities of Hawaiian soils and also of the further fact that the results of experiments made elsewhere with phosphate fertilizers, have been so contradictory that it is impossible to apply them to Hawaiian conditions, it was deemed important and desirable to make a careful study of the solubility of the phosphoric acid naturally occurring in the soils as well as of the behavior of various phosphates when applied to them.

Investigations were therefore undertaken to determine the availability of the phosphoric acid in untreated and fertilized typical Hawaiian soils as well as the manner in which phosphates are locked up in the soil.[2] These investigations included several series of pot experiments. One series involved five successive crops and extended over a period of two and one-half years. In another three successive crops were raised. In connection with these experiments determinations were made of the total phosphoric acid in the soil, the percentage of phosphoric acid in the soil and in the various phosphates soluble in different solvents, and the quantities of phosphoric acid absorbed by the crops grown. The principal crops used in the experiments were millet, cowpeas, and buckwheat. Such experiments were considered necessary in order to be able to recommend the most economical form of phosphate to use on the peculiar soils of Hawaii.

[1] Hawaii Sta. Buls. 35 (1914) and 40 (1915).

[2] The pot experiments carried on in this work were first undertaken in cooperation with the Basic Slag Committee of the Association of the Official Agricultural Chemists, but have been continued and broadened to obtain information in regard to phosphate fertilizers for Hawaiian soils.

AVAILABILITY OF DIFFERENT PHOSPHATES APPLIED TO HAWAIIAN SOILS.

SOIL TYPES USED.

Three types of soil, one of which was thought to be very deficient in phosphoric acid were used. The following table shows the chemical composition of the soils as determined by digestion with hydrochloric acid of specific gravity 1.115:

TABLE I.—*Composition of soils used in the experiments.*

	Soil No. 1.	Soil No. 2.	Soil No. 3.
	Per cent.	*Per cent.*	*Per cent.*
Moisture	7.65	12.61	4.02
Volatile matter	8.42	12.19	15.33
Insoluble matter	38.49	36.74	31.60
Ferric oxid (Fe_2O_3)	16.63	15.96	21.28
Alumina (Al_2O_3)	12.85	17.52	21.37
Titanium oxid (TiO_2)	2.00	3.50	3.60
Manganese oxid (Mn_3O_4)	.24	.08	.20
Lime (CaO)	1.84	.18	.50
Magnesia (MgO)	8.71	.34	.64
Potash (K_2O)	.39	.34	.35
Soda (Na_2O)	1.36	.28	.35
Sulphur trioxid (SO_3)	.08	.44	.32
Phosphoric acid (P_2O_5)	.57	.28	.29

Soil No. 1 represents the type to be found in and about Honolulu. It has a sandy texture and is derived in part from the disintegration of black volcanic ash. It is used for truck gardening, rice, and bananas.

Soil No. 2 is the highly ferruginous type of red clay so abundant in the islands.

Soil No. 3 is a red soil very similar to No. 2, differing in that No. 3 has a better texture, that is, less clay.

METHOD.

The method used in preparing the pots was similar to that proposed by the Basic Slag Committee of the Association of Official Agricultural Chemists. Tin pots were used instead of clay pots in order to eliminate the loss of fertilizer through efflorescence. Each pot contained 6 pounds of soil. The forms of phosphate used were: Double superphosphate (46.25 per cent P_2O_5), acid phosphate (19.49 per cent P_2O_5), four different Thomas phosphate slags (A, 18.38 per cent P_2O_5; B, 19.04 per cent P_2O_5; C, 13.31 per cent P_2O_5; D, 15.86 per cent P_2O_5), phosphate rock (29.4 per cent P_2O_5), commercial sodium phosphate (20.87 per cent P_2O_5), trimagnesium phosphate (54.1 per cent P_2O_5), tribasic potassium phosphate (33.4 per cent P_2O_5), dibasic potassium phosphate (40.8 per cent P_2O_5), monobasic potassium phosphate (52.2 per cent P_2O_5), reverted phosphate (18.56 per cent P_2O_5), bone meal (27.76 per cent P_2O_5), ferrous phosphate (37.8 per cent P_2O_5), ferric phosphate (31.8 per cent P_2O_5), aluminum phosphate (58 per cent P_2O_5), and titanium phosphate (34.1 per cent

P_2O_5). All phosphates were ground to about the same degree of fineness. Each pot received an application of nitrogen as sodium nitrate and blood, potash as potassium sulphate, and lime as calcium carbonate. The lime was added to counterbalance any influences which the basic material in the slag might exert, and was added in excess of the lime requirement as determined by the Veitch method.

The crops used included Japanese millet, cowpeas, buckwheat, radishes, and turnips.

Fertilizer applications are represented in the table as follows:

N = 0.06 per cent nitrogen from blood and 0.01 per cent from sodium nitrate.

$N_{1½}$ = 0.09 per cent nitrogen from blood and 0.015 per cent from sodium nitrate.

K = 0.10 per cent potash (K_2O) from potassium sulphate.

$K_{1½}$ = 0.15 per cent potash from potassium sulphate.

Ca = 0.10 per cent calcium carbonate plus that required by the Veitch method.

Ca_x = 0.15 per cent calcium carbonate plus that required by the Veitch method.

$P_{½}$ = 0.007 per cent phosphoric acid (P_2O_5) from the phosphate indicated.

P_1, $P_{1½}$, P_2 = 0.014, 0.021, and 0.028 per cent phosphoric acid, respectively.

L = legumes.

In one series of the experiments, green manure in the form of well-macerated cowpea vines was added at the rate of 2 ounces per pot; in the other no green manure was added. All applications were made in duplicate two weeks before seeding. The pots were watered daily.

EXPERIMENT I.

In the first experiment, soil No. 2 was used, a heavy clay soil very deficient in available phosphoric acid. In Table II are given the numbers of the pots, kind and amount of fertilizer added, weight of crop both green and dry, weight of heads, and plants per two pots. The first crop, Japanese millet, was planted July 31 and harvested October 20. The soil was then dried out, aerated, returned to the pots, and planted to cowpeas November 17. This crop was cut on January 17, weighed (each pot separately), and returned to the respective pots. Without any further addition of fertilizer the pots were planted to buckwheat February 6, which crop was harvested March 27. The soil was again dried out, well aerated, and again planted to millet May 18, without further addition of fertilizer. This crop was harvested on August 10. The soil was again dried, aerated, and well mixed as above, and after a full application of nitrogen and potash, but no phosphoric acid, was again planted to millet.

TABLE II.—*Effect of fertilizers on weight of crops in Experiment I.*

Pot Nos.	Fertilizer added.	Millet I.				Cowpeas.		Buckwheat.			Millet II.				Millet III.		
		Weight of crop.			Number of plants.	Weight of crop, green.	Number of plants.	Weight of crop.		Number of plants.	Weight of crop.			Number of plants.	Weight of crop.		Number of plants.
		Green.	Dry.	Heads.				Green.	Dry.		Green.	Dry.	Heads.		Green.	Dry.	
		Grams.	*Grams.*	*Grams.*		*Grams.*		*Grams.*	*Grams.*		*Grams.*	*Grams.*	*Grams.*		*Grams.*	*Grams.*	
1, 2	N-K-Ca-L	46	18.5	4.5	8	43.2	8	22.0	10.0	8	45.5	22.7	4.8	8	7.2	4.0	2
5, 6	N-K-Ca	32	13.0	4.0	7	43.9	8	24.0	.....	8	50.5	25.0	4.9	8	.....	.....	.....
9, 10	N-K-Ca-L	27	12.5	3.0	3	46.0	8	24.5	10.2	8	59.5	27.4	6.4	8	8.5	5.0	4
13, 14	N-K-Ca	20	10.0	2.5	4	50.6	8	28.0	11.9	8	61.2	27.3	6.0	9	9.1	6.0	2
17, 18	N-K-Ca-L-$P_{1/2}$ (slag A)	35	12.0	2.0	5	70.4	8	34.0	13.2	8	77.5	36.3	6.6	10	28.0	14.3	8
21, 22	N-K-Ca-$P_{1/2}$ (slag A)	44	16.0	4.0	6	69.4	8	39.5	14.5	8	76.0	33.7	6.3	10	17.2	9.2	8
25, 26	N-K-Ca-L-$P_{1/2}$ (slag B)	66	28.5	4.0	4	78.4	8	34.5	12.7	8	70.5	33.5	6.1	9	34.5	18.4	8
29, 30	N-K-Ca-$P_{1/2}$ (slag B)	87	34.0	6.0	8	78.3	8	41.5	14.8	8	68.0	32.1	6.0	9	39.0	20.0	8
33, 34	N-K-Ca-L-$P_{1/2}$ (slag C)	70	27.0	6.0	8	83.4	6	24.0	11.4	8	70.5	33.3	5.1	8	26.5	15.0	8
37, 38	N-K-Ca-$P_{1/2}$ (slag C)	74	29.0	6.0	8	83.0	8	40.5	16.3	8	72.0	32.5	5.9	10	47.0	21.3	8
41, 42	N-K-Ca-L-$P_{1/2}$ (slag D)	84	32.0	5.0	8	55.2	8	23.2	10.5	8	68.0	32.2	6.0	10	27.0	13.7	6
45, 46	N-K-Ca-$P_{1/2}$ (slag D)	90	39.0	8.5	8	70.5	8	39.5	14.8	8	63.0	29.0	5.5	10	52.0	25.3	8
49, 50	N-K-Ca-L-$P_{1/2}$ (acid phosphate)	119	45.0	10.0	8	43.5	8	26.5	11.3	8	38.5	17.5	3.1	5	12.5	6.5	4
53, 54	N-K-Ca-$P_{1/2}$ (acid phosphate)	125	50.0	12.0	8	65.2	8	45.5	16.9	8	69.2	31.7	6.6	9	9.7	6.5	8
57, 58	N-K-Ca-L-$P_{1/2}$ (phosphate rock)	12	6.0	1.0	3	64.0	8	42.7	16.1	8	76.5	34.4	7.3	10	7.5	2.5	3
61, 62	N-K-Ca-$P_{1/2}$ (phosphate rock)	28	11.5	2.5	8	59.2	8	39.5	14.7	8	68.7	29.9	5.6	9	.....	.....	.....
65, 66	N-K-Ca-L-$P_{1/2}$ (sodium phosphate).	102	37.0	8.0	7	75.0	8	42.5	14.8	8	76.0	33.1	6.6	10	20.5	12.0	8
69, 70	N-K-Ca-$P_{1/2}$ (sodium phosphate).	132	53.0	12.0	8	76.9	8	42.0	16.1	8	64.0	28.3	6.1	10	31.5	16.5	5
73, 74	N-K-Ca-L-P_1 (slag A)	107	39.0	9.0	6	87.2	8	50.0	16.4	8	80.3	36.5	6.7	10	28.3	15.0	5
77, 78	N-K-Ca-P_1 (slag A)	125	49.0	11.0	8	97.3	8	52.5	17.2	8	83.5	37.7	7.2	10	61.5	30.8	8
81, 82	N-K-Ca-L-P_1 (slag B)	95	34.0	9.0	8	98.1	8	47.0	16.3	8	80.0	36.6	7.0	10	58.0	27.5	8
85, 86	N-K-Ca-P_1 (slag B)	120	42.0	12.0	8	84.2	8	51.5	18.2	8	77.5	34.4	6.3	10	51.5	25.0	8
89, 90	N-K-Ca-L-P_1 (slag C)	115	44.0	10.5	7	42.5	4	50.0	17.4	8	80.0	35.2	6.4	10	31.3	16.0	6
93, 94	N-K-Ca-P_1 (slag C)	68	25.0	5.0	6	101.5	8	63.5	21.8	8	85.9	39.0	6.6	10	33.5	16.2	8
97, 98	N-K-Ca-L-P_1 (slag D)	110	43.0	11.0	8	92.4	8	35.0	13.5	8	86.5	39.2	7.5	10	26.0	8.2	8
101, 102	N-K-Ca-P_1 (slag D)	135	54.0	12.0	8	104.3	8	50.0	19.2	8	80.0	36.1	6.7	9	34.0	17.3	5
105, 106	N-K-Ca-L-P_1 (acid phosphate)	117	34.0	7.0	8	97.0	8	50.0	17.7	8	74.5	34.1	5.3	10	59.0	32.5	8
109, 110	N-K-Ca-P_1 (acid phosphate)	207	78.0	18.5	8	79.2	8	46.0	16.5	8	86.0	38.0	7.2	10	35.5	17.9	8
113, 114	N-K-Ca-L-P_1 (phosphate rock)	40	20.0	3.0	5	91.4	8	49.5	16.2	8	81.5	36.0	6.8	9	12.0	7.5	3
117, 118	N-K-Ca-P_1 (phosphate rock)	30	13.0	2.0	6	84.2	8	47.5	16.0	8	80.5	35.0	6.7	10	20.6	10.5	8
121, 122	N-K-Ca-L-P_1 (sodium phosphate).	204	77.0	17.0	8	121.0	8	60.5	21.8	8	82.2	37.8	7.0	10	68.0	31.7	8
125, 126	N-K-Ca-P_1 (sodium phosphate)	214	85.0	17.0	8	85.1	8	51.5	16.8	8	84.1	37.5	6.7	10	44.5	19.5	8
129, 130	N-K-Ca_x-L-P_1 (sodium phosphate).	104	37.0	9.0	6	75.2	8	46.0	17.2	8	78.5	37.0	5.7	9	38.4	18.0	8
133, 134	N-K-Ca_x-P_1 (sodium phosphate)	169	70.0	14.0	8	109.0	8	59.0	21.5	8	84.0	38.0	6.2	10	27.1	14.0	8

TABLE II.—*Effect of fertilizers on weight of crops in Experiment I*—Continued.

Pot Nos.	Fertilizer added.	Millet I.				Cowpeas.		Buckwheat.			Millet II.				Millet III.		
		Weight of crop.			Number of plants.	Weight of crop, green.	Number of plants.	Weight of crop.		Number of plants.	Weight of crop.			Number of plants.	Weight of crop.		Number of plants.
		Green.	Dry.	Heads.				Green.	Dry.		Green.	Dry.	Heads.		Green.	Dry.	
		Grams.	*Grams.*	*Grams.*		*Grams.*		*Grams.*	*Grams.*		*Grams.*	*Grams.*	*Grams.*		*Grams.*	*Grams.*	
137, 138.	$N_{1\ 1/2}$-$K_{1\ 1/2}$-Ca-L-P_1 (sodium phosphate).	97	36.0	9.0	5	124.0	8	56.0	19.6	8	87.0	40.0	6.8	10	14.0	8.5	4
141, 142.	$N_{1\ 1/2}$-$K_{1\ 1/2}$-Ca-P_1 (sodium phosphate).	210	82.0	19.0	8	63.2	8	39.0	14.4	8	60.5	17.0	3.9	6	15.5	9.0	4
145, 146.	N-K-Ca-L-$P_{1\ 1/2}$ (sodium phosphate).	217	79.0	18.0	7	143.7	8	70.0	22.0	8	78.5	34.9	6.2	10	62.5	32.1	8
149, 150.	N-K-Ca-$P_{1\ 1/2}$ (sodium phosphate).	189	78.0	15.5	7	106.4	8	61.5	20.7	8	97.0	38.7	6.7	10	47.0	21.5	7
153, 154.	N-K-Ca-L-P_2 (phosphate rock)..	102	42.0	10.0	8	120.7	8	58.0	21.2	8	85.5	38.2	6.0	10	47.8	23.0	8
157, 158.	N-K-Ca-P_2 (phosphate rock).....	13	6.0	1.0	1	89.8	8	40.5	15.5	8	77.5	34.5	6.5	10	19.3	10.0	5
161, 162.	N-K-Ca-L-$P_{1/2}$ (superphosphate)	59	25.0	5.0	3	93.5	8	52.5	18.9	8	83.5	37.8	5.9	9	33.0	16.5	8
165, 166.	N-K-Ca-$P_{1/2}$ (superphosphate)...	122	48.0	12.0	8	71.0	8	26.0	12.6	8	53.5	25.1	5.2	9	48.0	25.0	8
169, 170.	N-K-Ca-L-P_1 (superphosphate)	97	39.0	7.5	4	51.6	8	33.5	13.4	8	75.5	34.2	6.7	10	35.0	18.0	8
173, 174.	N-K-Ca-P_1 (superphosphate)....	186	69.0	19.0	8	65.0	8	36.5	14.8	8	70.5	32.1	6.4	10	.....	.....	.....
223, 224.	N-K-Ca-L-$P_{1/2}$ (reverted phosphate).	58	31.3	6.8	8	.....	.....	.....	.....	.....	.....	.....	.....	.....	30.5	15.5	8
225, 226.	N-K-Ca-$P_{1/2}$(reverted phosphate).	61.7	34.2	4.5	6	.....	.....	.....	.....	.....	.....	.....	.....	.....	41.5	20.0	8
227, 228.	N-K-Ca-L-$P_{1/2}$ (bone meal).....	43.1	25.0	5.2	5	.....	.....	.....	.....	.....	.....	.....	.....	.....	35.8	18.0	8
229, 230.	N-K-Ca-$P_{1/2}$ (bone meal).....	48.0	30.3	5.7	7	.....	.....	.....	.....	.....	.....	.....	.....	.....	31.8	16.8	8
231, 232.	N-K-Ca-L-P_1 (reverted phosphate).	87.8	51.1	8.5	10	.....	.....	.....	.....	.....	.....	.....	.....	.....	31.0	15.2	8
233, 234.	N-K-Ca-P_1 (reverted phosphate).	(1)	(1)	(1)	(1)	.....	.....	.....	.....	.....	.....	.....	.....	.....	31.5	16.3	8
235, 236.	N-K-Ca-L-P_1 (bone meal).....	36.0	18.5	3.7	8	.....	.....	.....	.....	.....	.....	.....	.....	.....	23.0	12.5	8
237, 238.	N-K-Ca-P_1 (bone meal).....	(1)	(1)	(1)	(1)	.....	.....	.....	.....	.....	.....	.....	.....	.....	(1)	(1)	(1)

[1] No crop.

In considering the above data, it is necessary to allow for seasonal variations. That is, while it is possible to obtain a good growth the whole year round, some months are more favorable for growth than others. Hence differences in the various crops may not necessarily be due to the action of the fertilizers alone. Nevertheless, the influence of the different fertilizers in the same series is comparative.

The data show that this soil was very deficient in phosphoric acid, since in nearly every instance an increase in weight of the millet plant followed the addition of phosphate (see Pls. I and II). When phosphoric acid was added at the rate of 0.007 per cent P_2O_5 ($\Gamma_{1/2}$), the soluble phosphates were the most effective. Phosphate rock was the least effective, while reverted phosphate, bone meal, and slag had an almost negligible influence. When phosphoric acid was added at the rate of 0.014 per cent P_2O_5 (P_1), practically the same relation applied. By comparing the pots with and without legumes, where no phosphate was added, plant growth seems to have been benefited by the use of green manure. When added with the phosphates, the green manure did not show a very active influence except in the case of phosphate rock, when a better yield was obtained with the use of legumes.

While an increase in growth of cowpeas was brought about by the use of phosphate fertilizer, there was no great regular variation due to the various phosphates. When applied at the rate of 0.007 per cent P_2O_5, the slags had the greatest influence. Applied at the rate of 0.014 per cent P_2O_5, sodium phosphate gave a higher yield than slags. The influence of acid phosphate, superphosphate, and phosphate rock was quite marked. The highest yield in this series was obtained through the use of sodium phosphate at the rate of 0.021 per cent P_2O_5.

With buckwheat, as with the two previous crops, a marked influence was exerted upon growth by all forms of phosphate. The relative effect of the different fertilizers was quite similar, that is, while the soluble fertilizers were apparently the most effective, the difference was very small. However, it may be safely said that 0.014 per cent P_2O_5 was more effective than 0.007 per cent, while 0.021 per cent and 0.028 per cent were still more effective.

The most important fact brought out in the second series of tests with millet was the marked increase in effectiveness shown by the phosphate rock and slags, which were about equal to the soluble phosphates. In all cases 0.014 per cent P_2O_5 produced a higher yield than 0.007 per cent. Attention is called to the fact that, when added at the rate of 0.007 per cent P_2O_5, the phosphate rock was the most effective. But when added in larger quantities, the soluble phosphates still maintain their superiority as regards effectiveness to such an extent that sodium phosphate added at the rate of 0.021 per cent P_2O_5

FIG. 1.—COMPARATIVE AVAILABILITY OF PHOSPHORIC ACID IN THREE TYPES OF SOIL; ONLY NITROGEN AND POTASH ADDED.

Left to right: First two pots, red-clay soil No. 2; second pair, red soil No. 3; third pair, sandy soil No. 1.

FIG. 2.—INFLUENCE OF SODIUM PHOSPHATE, EXPERIMENT I, MILLET I.

Left to right: Check pots; sodium phosphate at the rate of 0.007, 0.014, and 0.021 per cent P_2O_5.

FIG. 1.—COMPARATIVE INFLUENCE OF PHOSPHATES, EXPERIMENT I, MILLET I.

Left to right paired pots: Check; slag at rates of 0.007 and 0.014 per cent P_2O_5; acid phosphate, 0.014 per cent P_2O_5.

FIG 2.—COMPARATIVE INFLUENCE OF PHOSPHATES, EXPERIMENT I, MILLET I.

Left to right paired pots: Phosphate rock at rates of 0.007, 0.014, and 0.028 per cent P_2O_5; acid phosphate, 0.007 per cent P_2O_5.

produced a larger yield than phosphate rock at the rate of 0.028 per cent P_2O_5. This indicates the more immediately effective influence of soluble phosphates.

In view of the depressed growth of the preceding crop, it seemed imperative to make a second application of nitrogen and potash for the third millet crop in the same quantities as in the original formula. In this way it would be possible to measure further the cumulative effects of the phosphates and to determine if the decrease in growth was due to the exhaustion of available phosphate. The result of this test was a further decrease of growth, proving the removal of available phosphate. The effectiveness of phosphate rock was lowered considerably as compared with the previous crop. The influence of slags at this stage was the most important result on this crop. Other than the slags, the soluble phosphates were more effective than the insoluble ones.

After repeated failures to obtain a normal growth of turnips in the pots, due to insect attacks, experiment with this crop was abandoned. However, almost complete data for one series were obtained, and the results were very much in accord with the first crop of the millet series. Phosphate rock proved the least available, the other phosphates were much more effective and very similar in their action. All applications had a markedly beneficial influence upon the growth of the turnips, and the plants to which lime was added were much larger than those treated with lime and legumes. These pots were later planted to radishes, but through the ravages of insects and other causes the experiments with this plant were also abandoned.

After standing for about nine months in the pots, the soil was well mixed and again seeded, this time to millet, in order to determine the relative availability of the phosphates after allowing the soil to lie fallow. The results were rather surprising in that all pots produced a very poor growth, but the pots fertilized with phosphoric acid were in advance of the checks. When added at the rate of 0.007 per cent phosphoric acid, acid phosphate gave the highest yield, while phosphate rock was second. When applied at the rate of 0.014 per cent, sodium phosphate was best, closely followed by the slags, phosphate rock, and acid phosphate in the order given. Since only a small percentage of phosphoric acid could have been removed by the turnips, the stunted growth indicated the inability of the lime in the quantities added to retain the phosphates as calcium phosphate.

The plants from the first two crops of millet and the crop of buckwheat were analyzed, partly to determine the amount of phosphoric acid removed from the soil, and also to determine whether any relation existed between the types of phosphate used and the phosphate content of the grain or straw.

As a result it may be said that the three crops removed from the soil an amount of phosphate equal to that added. There were, however, a few exceptions, especially where phosphate rock was used. These results offer information regarding the stunted growth of the last crop of millet and the increased effectiveness of phosphate rock as compared with the soluble phosphates in the second crop.

The analyses furnish very little information regarding the variation in the phosphate content of the grain and straw. The percentage of phosphate in the grain was increased by the addition of phosphate fertilizer, regardless of its availability in some cases, while in others the reverse was true. The same may be said regarding the straw, there being no regularity in the analyses. The results are given in Table III:

TABLE III.—*Phosphoric acid content of grain and straw as influenced by phosphate fertilizers.*

Pot Nos.	Fertilizer added.	Millet I.		Buckwheat.		Millet II.	
		Grain.	Straw.	Grain.	Straw.	Grain.	Straw.
		Per ct.	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*
1,2	N-K-Ca-L	0.293	0.121	0.383	0.085	0.218	0.156
5,6	N-K-Ca	.399	.172	.404	.115	.180	.169
9,10	N-K-Ca-L	.250	.099	.413	.146	.337	.094
13,14	N-K-Ca	.425	.092	.433	.102	.208	.088
17,18	N-K-Ca-L-P 1/2 (slag A)	.454	.192	.483	.127	.368	.187
21,22	N-K-Ca-P 1/2 (slag A)	.592	.277	.638	.122	.237	.187
25,26	N-K-Ca-L-P 1/2 (slag B)	.392	.196	.503	.129	.356	.203
29,30	N-K-Ca-P 1/2 (slag B)	.598	.209	.515	.156	.274	.230
33,34	N-K-Ca-L-P 1/2 (slag C)	.395	.173	.453	.175	.365	.293
37,38	N-K-Ca-P 1/2 (slag C)	.619	.263	.478	.116	.361	.263
41,42	N-K-Ca-L-P 1/2 (slag D)	.333	.116	.488	.133	.350	.253
45,46	N-K-Ca-P 1/2 (slag D)	.464	.157	.408	.115	.325	.230
49,50	N-K-Ca-L-P 1/2 (acid phosphate)	.350	.135	.462	.119	.236	.173
53,54	N-K-Ca-P 1/2 (acid phosphate)	.376	.126	.616	.128	.249	.179
57,58	N-K-Ca-L-P 1/2 (phosphate rock)	.....	.219	.472	.116	.283	.168
61,62	N-K-Ca-P 1/2 (phosphate rock)	.584	.240	.562	.202	.299	.120
65,66	N-K-Ca-L-P 1/2 (sodium phosphate)	.300	.179	.443	.118	.368	.144
69,70	N-K-Ca-P 1/2 (sodium phosphate)	.278	.133	.509	.136	.406	.119
73,74	N-K-Ca-L-P 1 (slag A)	.229	.077	.593	.238	.349	.114
77,78	N-K-Ca-P 1 (slag A)	.200	.079	.645	.152	.488	.108
81,82	N-K-Ca-L-P 1 (slag B)	.578	.108	.518	.114	.422	.158
85,86	N-K-Ca-P 1 (slag B)	.367	.051	.598	.185	.407	.128
89,90	N-K-Ca-L-P 1 (slag C)	.252	.097	.....	.101	.397	.139
93,94	N-K-Ca-P 1 (slag C)	.265	.134	.581	.099	.316	.148
97,98	N-K-Ca-L-P 1 (slag D)	.307	.143	.428	.097	.262	.106
101,102	N-K-Ca-P 1 (slag D)	.443	.171	.428	.068	.294	.098
105,106	N-K-Ca-L-P 1 (acid phosphate)	.584	.275	.617	.125	.502	.191
109,110	N-K-Ca-P 1 (acid phosphate)	.358	.162	.675	.346	.448	.163
113,114	N-K-Ca-L-P 1 (phosphate rock)	.345	.172	.498	.099	.314	.153
117,118	N-K-Ca-P 1 (phosphate rock)	.666	.....	.507	.124	.507	.130
121,122	N-K-Ca-L-P 1 (sodium phosphate)	.471	.209	.494	.104	.521	.148
125,126	N-K-Ca-P 1 (sodium phosphate)	.329	.224	.732	.188	.383	.140
129,130	N-K-Ca_x-L-P 1 (sodium phosphate)	.537	.336	.509	.119	.464	.129
133,134	N-K-Ca_x-P 1 (sodium phosphate)	.189	.153	.519	.099	.421	.154
137,138	N 1 1/2-K 1/2-Ca-L-P 1 (sodium phosphate	.377	.209	.538	.157	.387	.169
141,142	N 1 1/2-K 1 1/2-Ca-P 1 (sodium phosphate)	.277	.128	.680	.244	.452	.139
145,146	N-K-Ca-L-P 1 1/2 (sodium phosphate)	.421	.195	.657	.167	.547	.145
149,150	N-K-Ca-P 1 1/2 (sodium phosphate)	.510	.260	.752	.219	.672	.106
153,154	N-K-Ca-L-P 2 (phosphate rock)	.444	.216	.650	.169	.672	.104
157,158	N-K-Ca-P 2 (phosphate rock)	.....	.....	.764	.246	.428	.115
161,162	N-K-Ca-L-P 1/2 (superphosphate)	.351	.169	.652	.120	.598	.105
165,166	N-K-Ca-P 1/2 (superphosphate)	.296	.123	.576	.182	.448	.109
169,170	N-K-Ca-L-P 1 (superphosphate)	.388	.221	.682	.159	.349	.081
173,174	N-K-Ca-P 1 (superphosphate)	.369	.135	.522	.139	.627	.104

EXPERIMENT II.

Another series of experiments with millet was made with this same type of soil—namely, No. 2—the results of which are given in Table IV. Fertilizers were added in the same amounts as in the previous series, and the soil was otherwise given similar treatment. This was deemed necessary to verify some of the results obtained in the first series. After the second crop of millet, a complete fertilizer was added before the planting of the third crop. (See Pls. III and IV.)

TABLE IV.—*Effect of fertilizers on weight of crops in Experiment II.*

Pot Nos.	Fertilizer added.	Millet I.			Millet II.				Millet III.[1]		
		Weight of crop.		Number of plants.	Weight of crop.			Number of plants.	Weight of crop.		Number of plants.
		Green.	Dry.		Green.	Dry.	Heads.		Green.	Dry.	
		Gm.	*Gm.*		*Gm.*	*Gm.*	*Gm.*		*Gm.*	*Gm.*	
1,2	N-K-Ca-L	8.1	4.6	3	51.5	24.6	6.4	8	.....	.....	.....
5,6	N-K-Ca	(2)	.....	.....	(2)	.....	.....	.....	14.1	8.3	5
9,10	N-K-Ca-L	2.0	.9	2	53.0	24.3	6.3	7	14.8	8.0	4
13,14	N-K-Ca	.9	.2	1	23.0	10.0	2.25	8	15.9	9.0	4
17,18	N-K-Ca-L-P 1/2 (slag A)	23.4	15.5	8	63.6	30.4	7.2	7	66.4	32.1	8
21,22	N-K-Ca-P 1/2 (slag A)	23.9	13.8	8	98.9	45.2	11.1	8	65.2	30.8	8
25,26	N-K-Ca-L-P 1/2 (slag B)	28.5	18.4	8	89.0	39.5	10.3	8	94.1	49.2	8
29,30	N-K-Ca-P 1/2 (slag B)	27.5	19.0	8	79.5	41.6	8.8	8	113.5	49.5	8
33,34	N-K-Ca-L-P 1/2 (slag C)	20.5	12.8	7	101.0	44.5	9.3	8	83.5	42.5	8
37,38	N-K-Ca-P 1/2 (slag C)	11.7	7.6	5	83.0	38.2	8.2	8	77.5	37.5	8
41,42	N-K-Ca-L-P 1/2 (slag D)	23.3	15.0	7	64.0	34.0	8.4	8	13.5	7.5	2
45,46	N-K-Ca-P 1/2 (slag D)	14.0	8.4	6	63.6	30.0	7.2	8	92.5	47.0	8
49,50	N-K-Ca-L-P 1/2 (acid phosphate)	33.7	24.8	8	55.5	27.1	5.6	8	84.1	41.5	8
53,54	N-K-Ca-P 1/2 (acid phosphate)	34.5	23.8	6	46.2	23.9	4.8	8	87.2	40.7	8
57,58	N-K-Ca-L-P 1/2 (phosphate rock)	18.7	12.3	4	100.0	45.6	9.6	8	11.6	5.5	4
61,62	N-K-Ca-P 1/2 (phosphate rock)	(2)	.....	.....	68.5	30.5	8.8	9	27.5	12.7	4
65,66	N-K-Ca-L-P 1/2 (sodium phosphate)	54.0	37.4	7	95.0	41.6	6.1	6	90.4	43.0	8
69,70	N-K-Ca-P 1/2 (sodium phosphate)	40.4	25.9	8	57.6	29.3	5.3	8	85.7	41.5	5
73,74	N-K-Ca-L-P 1 (slag A)	32.7	21.1	6	79.0	35.0	4.0	6	66.5	29.0	4
77,78	N-K-Ca-P 1 (slag A)	29.7	20.6	8	108.5	48.0	4.6	5	103.7	50.2	8
81,82	N-K-Ca-L-P 1 (slag B)	30.7	20.9	7	98.0	43.2	7.7	7	122.4	43.5	8
85,86	N-K-Ca-P 1 (slag B)	35.5	24.7	8	101.0	46.5	5.2	6	111.7	49.0	8
89,90	N-K-Ca-L-P 1 (slag C)	33.7	21.6	8	85.6	40.0	7.8	8	72.5	30.5	4
93,94	N-K-Ca-P 1 (slag C)	16.5	9.7	7	102.0	45.1	8.4	7	125.5	61.0	8
97,98	N-K-Ca-L-P 1 (slag D)	24.2	18.5	7	80.0	36.0	8.1	8	72.5	35.5	4
101,102	N-K-Ca-P 1 (slag D)	11.0	7.0	2	86.0	40.5	8.3	8	117.0	54.6	8
105,106	N-K-Ca-L-P 1 (acid phosphate)	39.0	26.9	8	95.5	43.7	6.5	7	122.2	52.0	8
109,110	N-K-Ca-P 1 (acid phosphate)	41.5	28.3	7	77.0	35.0	6.2	8	66.7	33.0	4
113,114	N-K-Ca-L-P 1 (phosphate rock)	17.0	10.9	6	97.0	43.2	8.3	7	30.5	15.5	8
117,118	N-K-Ca-P 1 (phosphate rock)	8.9	5.8	4	76.0	36.0	8.1	8	17.2	8.5	8
121,122	N-K-Ca-L-P 1 (sodium phosphate)	42.5	26.0	8	108.0	48.8	6.0	8	120.7	55.5	8
125,126	N-K-Ca-P 1 (sodium phosphate)	65.0	43.3	8	90.0	41.5	5.9	8	68.5	28.3	4
129,130	N-K-Ca-L-P 1 (sodium phosphate)	45.5	32.2	7	90.5	47.7	8.1	9	113.7	49.4	8
133,134	N-K-Ca-P 1 (sodium phosphate)	61.0	39.2	8	92.0	45.0	7.0	8	115.7	52.5	8
137,138	N 1 1/2 K 1 1/2 Ca-L-P 1 (sodium phosphate)	27.2	17.7	4	86.5	41.4	10.1	8	71.0	25.8	8
141,142	N 1 1/2 K 1 1/2 Ca-P 1 (sodium phosphate)	37.0	22.8	5	110.5	51.6	11.0	9	77.5	33.3	8
145,146	N-K-Ca-L-P 1 1/2 (sodium phosphate)	42.5	34.4	8	116.0	52.6	8.3	8	141.2	59.3	8
149,150	N-K-Ca-P 1 1/2 (sodium phosphate)	48.2	32.2	7	113.5	50.7	9.3	8	157.2	73.0	8

[1] Complete reapplication of fertilizer.

[2] No crop.

TABLE IV.—*Effect of fertilizers on weight of crops in Experiment II*—Continued.

Pot Nos.	Fertilizer added.	Millet I.			Millet II.				Millet III.		
		Weight of crop.		Number of plants.	Weight of crop.			Number of plants.	Weight of crop.		Number of plants.
		Green.	Dry.		Green.	Dry.	Heads.		Green.	Dry.	
153,154.	N-K-Ca-L-P_2 (phosphate rock)	*Gm.* 16.7	*Gm.* 11.7	5	*Gm.* 98.5	*Gm.* 44.2	*Gm.* 9.4	8	*Gm.* 34.5	*Gm.* 17.0	4
157,158.	N-K-Ca-P_2 (phosphate rock)	(1)	.....	.....	87.5	39.1	8.7	8	66.8	30.0	8
161,162.	N-K-Ca-L-$P_{1/2}$ (superphosphate)	40.7	26.6	7	61.0	38.1	5.6	8	131.9	63.8	8
165,166.	N-K-Ca-$P_{1/2}$ (superphosphate)	30.5	21.5	7	44.5	22.7	3.6	8	78.4	40.5	6
169,170.	N-K-Ca-L-P_1 (superphosphate)	46.5	30.0	7	89.5	45.0	7.4	7	149.6	70.2	8
173,174.	N-K-Ca-P_1 (superphosphate)	48.5	32.7	7	79.5	36.8	6.3	8	117.5	57.6	8

[1] No crop.

The first crop was planted February 2 and harvested May 2, the second crop planted May 8 and harvested August 10, and the third crop planted October 12 and harvested January 6. The soil was well mixed, aerated, and dried in the air for a short time between plantings.

The results of the first series were almost completely verified by this second planting. The pots to which no phosphate was added produced a very poor growth. All applications of phosphate increased the growth, the soluble phosphates having the greatest influence, while phosphate rock had the least.

The second crop of millet in this series again verified the results of the first series with marked regularity. When added at the rate of 0.007 per cent P_2O_5, phosphate rock and the slags were most efficient. The availability of the phosphate rock when added at the rate of 0.014 per cent P_2O_5, was very high, but did not surpass that of sodium phosphate, and the latter, when added at the rate of 0.021 per cent P_2O_5, produced a heavier growth than the former when added at the rate of 0.028 per cent P_2O_5. This apparently is further evidence of the more lasting effect of phosphate rock when added in small quantities, and of the superiority of the soluble phosphates when added in larger quantities.

At the same time that the pots in Experiment I were ready for the third planting of millet those in Experiment II were also ready for the third crop of millet. In view of this fact, another complete application of nitrogen and potash was made in the former with the results already given, while a second application of phosphate was made to the latter in order to compare the two. The most obvious results were the rapidity of growth in Experiment II as compared with that in Experiment I and the increase in weight of plants at

FIG. 1.—COMPARATIVE INFLUENCE OF PHOSPHATES, EXPERIMENT II, MILLET I.

Left to right: Check; slag, phosphate rock, acid phosphate, superphosphate, and sodium phosphate, each used at the rate of 0.014 per cent P_2O_5.

FIG. 2.—COMPARATIVE INFLUENCE OF PHOSPHATES, EXPERIMENT II, MILLET I.

Left to right paired pots: Check, phosphate rock at rates of 0.007, 0.014, and 0.028 per cent P_2O_5.

FIG. 1.—COMPARATIVE INFLUENCE OF PHOSPHATES, EXPERIMENT II, MILLET I.

Left to right paired pots: Check; sodium phosphate at rates of 0.007, 0.014, and 0.021 per cent P_2O_5.

FIG. 2.—INFLUENCE OF COWPEAS ON THE AVAILABILITY OF PHOSPHATE ROCK, EXPERIMENT II, MILLET I.

Left to right paired pots: Phosphate rock at the rate of 0.007 per cent P_2O_5 without cowpeas; same with cowpeas; phosphate rock 0.014 per cent P_2O_5 without cowpeas; same with cowpeas.

maturity. Phosphate rock again, as in the original application, proved the least available. The other phosphates were quite similar in their action, and all were more effective than phosphate rock. Large applications of the latter were little more effective than small applications.

EXPERIMENT III.

In view of the fact that the soil used in Experiments I and II was deficient in phosphoric acid, two soils less deficient in this constituent and of a much better mechanical texture were chosen for further tests. In soil No. 1 the phosphates had little influence upon plant growth, for which reason only one planting was made. In soil No. 3 there was a slight effect, and two crops were grown in this series. In the red clay soil (No. 2), the plants did not stool, but in soils Nos. 1 and 3 there was excessive stooling, and for this reason the number of stools as well as of plants is indicated in the tables.

The treatment of the pots was somewhat modified as follows: Only one slag was used in this series, and additions were made of trimagnesium phosphate, tripotassium phosphate, dipotassium phosphate, monopotassium phosphate, reverted phosphate, and bone meal.

The pots of soil No. 1 were seeded June 18 and harvested September 10. Those of soil No. 3 were seeded June 23 and harvested September 18; they were then aerated, mixed, and replanted to millet October 12, and harvested January 11. The results are given in Table V.

All pots of soil No. 1 produced an excellent growth of millet regardless of fertilizer. The growth in the pots containing sodium phosphate was slightly greater than in the other pots, but this soil showed itself to be very high in available phosphate.

Soil No. 3 proved to be slightly deficient in available phosphoric acid, and an increase in plant growth resulted from all phosphate applications. Phosphate rock was again the least effective of all the phosphates. Sodium phosphate and superphosphate produced the largest increase, while the results from slags and acid were very good. Reverted phosphate and bone meal were very ineffective. The monobasic, dibasic, and tribasic potassium phosphates were used to determine, if possible, any influence due to basicity of the salt, but no such relation was apparent.

The second millet crop on soil No. 3 gave very little information of additional value. In this crop the plants did not stool, and partly for this reason the weight of the plants was considerably reduced; hence the decrease in plant growth noted here must be attributed primarily to seasonal factors, although removal of readily available phosphate may have been a minor factor. Phosphate rock proved to be a very ineffective form of phosphate, and the soluble phosphates gave the best results.

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TABLE V.—*Effect of fertilizers on weight of crops in Experiment III.*

Pot Nos.	Fertilizer added.	Soil No. 1.						Soil No. 3.									
		Millet.						Millet I.						Millet II.			
		Weight of crop.			Number of plants.	Number of stools.	Number of heads.	Weight of crop.			Number of plants.	Number of stools.	Number of heads.	Weight of crop.		Number of plants.	Number of heads.
		Green.	Dry.	Heads.				Green.	Dry.	Heads.				Green.	Dry.		
		Grams.	*Grams.*	*Grams.*				*Grams.*	*Grams.*	*Grams.*				*Grams.*	*Grams.*		
1,2	N-K-Ca-L	263.0	120.0	28.2	7	16	16	89.0	50.5	9.3	8	.....	8	25.5	14.5	8	8
5,6	N-K-Ca	236.0	108.0	19.0	8	17	17	15.5	10.0	.6	4	.....	2	38.0	19.8	8	8
9,10	N-K-Ca-L	268.0	126.5	22.2	8	14	14	93.0	43.5	8.5	6	.....	6	29.5	17.8	8	8
13,14	N-K-Ca	251.0	120.0	15.8	8	12	12	(1)	.....	.....	.....	.....	.....	(1)	.....	.....	.....
17,18	N-K-Ca-L-$P_{1/2}$ (slag A)	283.0	129.1	15.4	8	19	19	174.0	87.5	19.0	8	9	8	39.0	21.3	8	8
21,22	N-K-Ca-$P_{1/2}$ (slag A)	244.0	109.5	13.6	8	13	14	148.0	76.0	14.8	9	.....	9	30.0	16.2	8	8
49,50	N-K-Ca-L-$P_{1/2}$ (acid phosphate)	208.0	112.0	18.8	8	11	11	155.0	83.5	16.9	7	.....	7	46.0	24.4	8	8
53,54	N-K-Ca-$P_{1/2}$ (acid phosphate)	217.0	93.5	11.4	7	11	10	151.0	79.0	12.7	9	.....	7	29.0	15.5	8	8
57,58	N-K-Ca-L-$P_{1/2}$ (phosphate rock)	255.0	123.0	22.3	7	16	15	129.0	71.7	14.4	8	9	8	36.0	19.9	8	8
61,62	N-K-Ca-$P_{1/2}$ (phosphate rock)	269.0	110.5	15.5	8	15	15	17.0	9.5	1.1	3	.....	3	41.3	22.6	8	8
65,66	N-K-Ca-L-$P_{1/2}$ (sodium phosphate)	255.0	124.5	21.8	8	20	19	166.0	84.0	15.0	8	9	9	37.5	20.7	8	8
69,70	N-K-Ca-$P_{1/2}$ (sodium phosphate)	263.0	121.7	26.0	8	21	22	180.0	89.0	14.5	8	.....	8	45.5	24.9	8	8
73,74	N-K-Ca-L-P_1 (slag A)	209 0	86.0	15.6	8	13	12	179.0	92.0	14.6	8	.....	8	73.0	42.5	8	8
77,78	N-K-Ca-P_1 (slag A)	229.0	96.0	19.6	7	14	14	161.0	83.5	11.0	8	.....	6	48.8	27.7	8	8
105,106	N-K-Ca-L-P_1 (acid phosphate)	236.0	97.0	15.8	8	13	12	160.0	93.0	13.2	8	10	10	61.1	35 5	8	8
109,110	N-K-Ca-P_1 (acid phosphate)	257.0	100 5	17.5	8	14	14	160.0	91.6	8.9	8	9	7	37.0	20.2	8	8
113,114	N-K-Ca-L-P_1 (phosphate rock)	258.0	102.0	15.3	8	13	11	35.0	21.1	2.5	3	4	4	43.2	22.7	8	8
117,118	N-K-Ca-P_1 (phosphate rock)	230.0	85.0	12.8	8	11	9	6.0	4.0	.5	5	.....	2	26.5	14.3	8	8
121,122	N-K-Ca-L-P_1(sodium phosphate)	284.0	103.0	16.5	8	15	13	209.0	104.8	13.1	9	11	9	46.5	24.9	8	8
125,126	N-K-Ca-P_1 (sodium phosphate)	230.0	93.0	14.3	8	.....	8	203.0	120.0	8.6	8	11	7	36.0	20.3	8	8
129,130	N-K-Ca_x-L-P_1 (sodium phosphate)	261.0	113.0	18.5	8	14	14	234.0	108.8	14.3	7	11	10	55.5	30.8	8	8
133,134	N-K-Ca_x-P_1 (sodium phosphate)	304.0	121.6	20.3	8	18	18	241.0	112.8	15.6	8	9	8	35.5	19.5	8	8
137,138	$N_{1\,1/2}$-$K_{1\,1/2}$-Ca-L-P_1 (sodium phosphate)	224.0	103.6	25.0	8	20	20	203.0	91.8	13.9	8	14	11	81.8	42.5	8	8
141,142	$N_{1\,1/2}$-$K_{1\,1/2}$-Ca-P_1 (sodium phosphate)	317.0	139.0	29.6	8	18	18	241.0	109.8	17.4	8	11	11	59.0	34.0	8	8
145,146	N-K-Ca-L-$P_{1\,1/2}$ (sodium phosphate)	291.0	99.7	19.5	8	17	16	237.0	112.8	14.5	8	18	17	78.0	46.7	8	8
149,150	N-K-Ca-$P_{1\,1/2}$(sodium phosphate)	211.0	89.0	17.5	8	15	12	236.0	108.0	16.0	8	18	16	37.0	32.7	8	8
153,154	N-K-Ca-L-P_2 (phosphate rock)	261.0	106.1	19.3	8	15	15	94.0	44.6	5.0	8	.....	4	27.7	16.7	8	8

[1] No crop.

TABLE V.—*Effect of fertilizers on weight of crops in Experiment III*—Continued.

Pot Nos.	Fertilizer added.	Soil No. 1.						Soil No. 3.									
		Millet.						Millet I.						Millet II.			
		Weight of crop.			Number of plants.	Number of stools.	Number of heads.	Weight of crop.			Number of plants.	Number of stools.	Number of heads.	Weight of crop.		Number of plants.	Number of heads.
		Green.	Dry.	Heads.				Green.	Dry.	Heads.				Green.	Dry.		
		Grams.	*Grams.*	*Grams.*				*Grams.*	*Grams.*	*Grams.*				*Grams.*	*Grams.*		
157, 158.	N-K-Ca-P_2 (phosphate rock)	244.0	97.0	17.5	8	14	14	(1)	.....	.....	.....	.....	.....	38.0	19.3	8	8
161, 162.	N-K-Ca-L-$P_{1/2}$ (superphosphate)	228.0	90.5	8.4	7	11	10	149.0	80.7	4.2	8	.....	3	30.4	13.5	8	8
165, 166.	N-K-Ca-$P_{1/2}$ (superphosphate)	258.0	106.0	15.7	8	15	14	145.0	74.4	5.7	8	.....	5	31.3	16.1	8	8
169, 170.	N-K-Ca-L-P_1 (superphosphate)	271.0	106.5	17.8	8	15	13	216.0	96.0	12.5	8	9	7	61.5	34.4	8	8
173, 174.	N-K-Ca-P_1 (superphosphate)	215.0	96.1	17.0	8	13	13	217.0	99.5	3.5	8	10	3	54.5	30.5	8	8
175, 176.	N-K-Ca-L-$P_{1/2}$ (trimagnesium phosphate)	258.0	111.7	17.6	7	13	12	184.0	92.0	12.6	9	.....	8	38.2	20.5	8	8
177, 178.	N-K-Ca-$P_{1/2}$ (trimagnesium phosphate)	294.0	120.0	18.8	8	16	15	136.0	68.3	9.7	8	.....	7	31.5	16.8	8	8
179, 180.	N-K-Ca-L-$P_{1/2}$ (tripotassium phosphate)	310.0	129.0	30.2	8	16	15	36.0	19.0	2.2	2	.....	1	50.5	27.5	8	8
181, 182.	N-K-Ca-$P_{1/2}$ (tripotassium phosphate)	264.0	125.0	31.0	8	19	15	160.0	78.5	11.8	8	.....	8	33.1	20.0	8	8
183, 184.	N-K-Ca-L-$P_{1/2}$ (dipotassium phosphate)	170.0	91.0	19.3	8	14	13	165.0	81.2	9.2	8	.....	6	57.5	33.7	8	8
185, 186.	N-K-Ca-$P_{1/2}$ (dipotassium phosphate)	264.0	113.0	22.0	8	22	20	152.0	76.0	11.8	8	.....	8	36.0	20.9	8	8
187, 188.	N-K-Ca-L-$P_{1/2}$ (monopotassium phosphate)	198.0	96.0	18.1	8	13	12	163.0	80.3	3.5	8	14	3	44.5	29.1	8	8
189, 190.	N-K-Ca-$P_{1/2}$ (monopotassium phosphate)	260.0	116.0	23.4	8	15	15	171.0	77.8	5.6	8	9	4	42.5	23.3	8	8
191, 192.	N-K-Ca-L-P_1 (trimagnesium phosphate)	95.0	47.0	8.5	4	5	5	155.0	75.5	1.2	7	8	1	32.0	28.2	8	8
193, 194.	N-K-Ca-P_1 (trimagnesium phosphate)	278.0	121.8	22.1	8	18	18	117.0	54.7	.....	8	.....	.....	36.5	25.0	8	8
195, 196.	N-K-Ca-L-P_1 (tripotassium phosphate)	180.0	89.0	16.5	8	12	12	214.0	89.5	4.5	8	11	3	32.5	24.0	8	8
197, 198.	N-K-Ca-P_1 (tripotassium phosphate)	288.0	125.0	26.8	8	19	19	193.0	85.0	2.0	8	10	2	39.5	26.5	8	8
199, 200.	N-K-Ca-L-P_1 (dipotassium phosphate)	233.0	118.5	20.2	8	19	18	198.0	93.5	9.2	7	10	6	53.8	32.0	8	8
201, 202.	N-K-Ca-P_1 (dipotassium phosphate)	291.0	134.0	28.7	8	21	21	213.0	100.0	9.1	8	12	6	42.0	26.0	8	8

TABLE V.—*Effect of fertilizers on weight of crops in Experiment III*—Continued.

Pot Nos.	Fertilizer added.	Soil No. 1.						Soil No. 3.									
		Millet.						Millet I.						Millet II.			
		Weight of crop.			Number of plants.	Number of stools.	Number of heads.	Weight of crop.			Number of plants.	Number of stools.	Number of heads.	Weight of crop.		Number of plants.	Number of heads.
		Green.	Dry.	Heads.				Green.	Dry.	Heads.				Green.	Dry.		
		Grams.	*Grams.*	*Grams.*				*Grams.*	*Grams.*	*Grams.*				*Grams.*	*Grams.*		
203, 204.	N-K-Ca-L-P_1 (monopotassium phosphate)	247.0	122.0	24.5	8	20	20	176.0	86.0	12.6	8	10	10	55.0	35.5	8	8
205, 206.	N-K-Ca-P_1 (monopotassium phosphate)	265.0	127.5	30.5	8	18	19	194.0	83.5	12.5	8	10	10	43.8	28.2	8	8
223, 224.	N-K-Ca-L-$P_{1/2}$ (reverted phosphate)	.....	.....	.....	.....	.....	.....	78.6	45.5	8.2	.....	6	6	41.0	26.5	8	8
225, 226.	N-K-Ca-$P_{1/2}$(reverted phosphate)	.....	.....	.....	.....	.....	.....	75.2	44.4	6.5	.....	9	8	32.1	21.0	8	8
227, 228.	N-K-Ca-L-$P_{1/2}$ (bone meal)	.....	.....	.....	.....	.....	.....	47.0	30.5	4.0	8	8	8	42.3	29.8	8	8
229, 230.	N-K-Ca-$P_{1/2}$ (bone meal)	.....	.....	.....	.....	.....	.....	42.2	24.6	3.5	8	8	8	44.0	27.0	8	8
231, 232.	N-K-Ca-L-P_1 (reverted phosphate)	.....	.....	.....	.....	.....	.....	90.0	53.7	6.7	8	8	6	46.0	27.7	8	8
233, 234.	N-K-Ca-P_1 (reverted phosphate)	.....	.....	.....	.....	.....	.....	30.0	15.7	1.9	7	7	6	26.4	15.0	8	8
235, 236.	N-K-Ca-L-P_1 (bone meal)	.....	.....	.....	.....	.....	.....	45.5	24.9	4.0	8	8	8	31.5	17.0	8	8
237, 238.	N-K-Ca-P_1 (bone meal)	.....	.....	.....	.....	.....	.....	31.5	15.9	2.6	5	5	4	22.5	13.7	8	8

EXPERIMENT IV.

Hawaiian soils contain abnormally large quantities of iron and aluminum. Investigators have attributed the unavailability of phosphoric acid in soils directly to the presence of these two elements, and it is quite generally held that the presence of adequate amounts of lime will prevent phosphates from combining with iron and aluminum. The first series of pots in Experiment IV, therefore, was planned to determine what influence the lime has on the availability of phosphoric acid in the soils. This series of pots was divided into two main groups, one receiving no lime, the other being limed at the rate of 0.10 per cent calcium carbonate in excess of the lime requirement as determined by the Veitch method.

The same three soils were used in this series as in previous experiments. Some of the pots were green manured with legumes, as indicated in the second column. The data are presented in the same manner as in the previous tables. Only one crop of millet was grown in soil No. 1, but the tests upon soils Nos. 2 and 3 were repeated by a second planting. The results are given in Table VI.

The addition of lime to soil No. 1 caused only a slight increase in growth of the plants. Probably this was due to the high percentages of lime and magnesia already present in this soil.

In soil No. 3 a large increase followed the application of lime with the soluble phosphates, but not its application with phosphate rock. This indicates that lime assists the plants in assimilating phosphoric acid, but whether this is a chemical or physical phenomenon is yet to be proved.

In soil No. 2 the effect of lime was much more striking. Here the growth of millet was increased in every instance where lime was applied with the phosphates. This soil is a heavy clay type; No. 3 contains much less clay, and No. 1 the least clay. It is entirely possible that there is a relation between the influence of the lime and the amount of clay present in the soil. The most striking effect of the lime in case of soil No. 2 was upon the character of the plant. In all pots without lime, the millet came up in clumps like grass and grew to a height of only about 6 inches, while the addition of lime produced normal plants.

On replanting the millet in soils Nos. 2 and 3 the results were somewhat different. The lime had apparently lost its influence in most cases, more especially in soil No. 3, which contained less clay.

The second part of Experiment IV was planned to determine the availability of ferrous, ferric, and aluminum phosphates as compared with the other phosphates. Soils Nos. 2 and 3 were used in this work, the results of which are given in Table VII.

TABLE VI.—*Effect of fertilizers with and without lime.*

Pot Nos.	Fertilizer added.	Soil No. 1.						Soil No. 2.						Soil No. 3.					
		Millet.						Millet I.						Millet I.					
		Lime.			No lime.			Lime.			No lime.			Lime.			No lime.		
		Weight of crop.		Number of plants.	Weight of crop.		Number of plants.	Weight of crop.		Number of plants.	Weight of crop.		Number of plants.	Weight of crop.		Number of plants.	Weight of crop.		Number of plants.
		Green.	Dry.		Green.	Dry.		Green.	Dry.		Green.	Dry.		Green.	Dry.		Green.	Dry.	
		Gm.	*Gm.*		*Gm.*	*Gm.*		*Gm.*	*Gm.*		*Gm.*	*Gm.*		*Gm.*	*Gm.*		*Gm.*	*Gm.*	
113, 114 207, 208	N–K–L–P_1 (phosphate rock)	258.0	102.0	8	201.0	96.8	8	40.0	20.0	5	32.4	17.0	8	35.0	21.1	3	62.2	38.4	8
117, 118 209, 210	N–K–P_1 (phosphate rock)	230.0	85.0	8	252.0	108.7	8	30.0	13.0	6	30.3	15.5	8	6.0	4.0	5	44.9	21.0	7
105, 106 211, 212	N–K–L–P_1 (acid phosphate)	236.0	97.0	8	234.0	97.0	8	117.0	34.0	8	33.2	18.0	8	160.0	93.0	8	117.0	75.2	8
109, 110 213, 214	N–K–P_1 (acid phosphate)	257.0	100.5	8	224.0	99.4	8	207.0	78.0	8	51.3	26.8	8	160.0	91.6	8	109.4	73.3	8
121, 122 215, 216	N–K–L–P_1 (sodium phosphate)	284.0	103.0	8	213.0	104.8	7	204.0	77.0	8	34.5	17.5	8	209.0	104.8	9	145.7	72.0	8
125, 126 217, 218	N–K–P_1 (sodium phosphate)	230.0	93.0	8	241.0	111.2	8	214.0	85.0	8	28.2	14.6	8	203.0	120.0	8	98.6	52.7	8
9, 10 219, 220	N–K–L	268.0	126.5	8	223.0	91.5	6	46.0	18.5	8	28.7	14.5	8	89.0	50.5	8	53.7	26.8	6
13, 14 221, 222	N–K	251.0	120.0	8	234.0	106.7	8	32.0	13.0	7	16.0	8.4	4	15.5	10.0	4	29.6	16.0	8

TABLE VI.—*Effect of fertilizers with and without lime*—Continued.

Pot Nos.	Fertilizer added.	Soil No. 1.						Soil No. 2.						Soil No. 3.					
		Millet.						Millet II.						Millet II.					
		Lime.			No lime.			Lime.			No lime.			Lime.			No lime.		
		Weight of crop.		Number of plants.	Weight of crop.		Number of plants.	Weight of crop.		Number of plants.	Weight of crop.		Number of plants.	Weight of crop.		Number of plants.	Weight of crop.		Number of plants.
		Green.	Dry.		Green.	Dry.		Green.	Dry.		Green.	Dry.		Green.	Dry.		Green.	Dry.	
		Gm.	*Gm.*		*Gm.*	*Gm.*		*Gm.*	*Gm.*		*Gm.*	*Gm.*		*Gm.*	*Gm.*		*Gm.*	*Gm.*	
113, 114 207, 208	N–K–L–P_1 (phosphate rock)							12.0	7.5	3	29.0	13.8	8	43.2	22.7	8	53.5	31.7	8
117, 118 209, 210	N–K–P_1 (phosphate rock)							20.6	10.5	8	34.5	15.7	8	26.5	14.3	8	37.9	21.8	8
105, 106 211, 212	N–K–L–P_1 (acid phosphate)							59.0	32.5	8	44.0	20.3	8	61.1	35.5	8	78.7	47.8	8
109, 110 213, 214	N–K–P_1 (acid phosphate)							35.5	17.9	8	44.0	20.2	8	37.0	20.4	8	65.2	37.5	8
121, 122 215, 216	N–K–L–P_1 (sodium phosphate)							68.0	31.7	8	33.0	16.7	8	46.5	24.9	8	63.5	37.0	8
125, 126 217, 218	N–K–P_1 (sodium phosphate)							44.5	19.5	8	40.8	20.2	8	36.0	20.3	8	55.5	37.5	8
9, 10 219, 220	N–K–L							8.5	5.0	4	14.8	8.0	8	29.5	17.8	8	34.0	20.0	8
13, 14 221, 222	N–K							9.1	6.0	2	(1)			(1)			27.8	16.0	8

[1] No crop.

TABLE VII.—*Availability of iron and aluminum phosphates.*

Fertilizer added.	Soil No. 2.			Soil No. 3.		
	Weight of crop.		Number of plants.	Weight of crop.		Number of plants.
	Green.	Dry.		Green.	Dry.	
	Grams.	*Grams.*		*Grams.*	*Grams.*	
N-K-Ca-L-P (ferrous phosphate)	7.0	3.8	1	45.5	21.5	8
N-K-Ca-P (ferrous phosphate)	(1)			41.0	17.5	8
N-K-L-P (ferrous phosphate)				51.5	35.5	8
N-K-Ca-L-P (ferric phosphate)	42.5	18.6	8	55.0	28.0	8
N-K-Ca-P (ferric phosphate)	35.5	16.7	8	60.5	31.8	8
N-K-L-P (ferric phosphate)				88.5	55.3	8
N-K-Ca-L-P (aluminum phosphate)	35.0	15.8	7	11.3	5.3	2
N-K-Ca-P (aluminum phosphate)	35.5	16.7	7	70.0	33.3	8
N-K-L-P (aluminum phosphate)				16.0	9.5	7
N-K-Ca (check)	8.5	5.0	4	29.5	17.8	8
N-K-L (check)				34.9	20.0	8

[1] No crop.

In soil No. 2, ferrous phosphate apparently had a toxic influence upon the millet, while ferric and aluminum phosphate proved to be very available types of fertilizer. They were more readily available than phosphate rock, about equal to basic slag, but less readily assimilated than soluble phosphate.

In case of soil No. 3, ferrous phosphate produced a good growth, due probably in part to the fact that this soil is more open and the ferrous salt may have been oxidized to ferric phosphate. Hence it may be said that both the iron salts and the aluminum salt are available sources of phosphoric acid, more so in this type of soil than phosphate rock, about the same as reverted phosphate and bone meal, but less than the other phosphates.

In view of the action of lime upon the availability of the phosphates shown in the previous table (Experiment IV), pots were prepared to which the iron and aluminum phosphates were applied with and without lime. The results showed iron phosphates to be more available without lime in this type of soil. The opposite relations held for aluminum phosphate.

SAND CULTURES.

A further test of the phosphates was made in sand culture to determine more precisely the action of the salts when not under the influence of complex soil conditions. Eighteen pots of silica sand were prepared, to each of which equal weights of nitrogen and potash fertilizer were applied in addition to the following, which were run in duplicate: Ferrous, ferric, aluminum, sodium, titanium, and acid phosphates, phosphate rock, and slag. Two check pots received nitrogen and potash but no phosphoric acid. Each phosphate pot contained the same weight of phosphoric acid (P_2O_5).

After about two weeks the plants were growing most vigorously in the pots containing sodium and acid phosphates. Ferrous phosphate was very toxic at this stage, but the plants were able to survive and partly overcome the toxicity. After two months' growth phosphate rock and ferrous phosphate had produced the smallest plants. Ferric and aluminum phosphate had produced the most vigorous plants, the former being slightly better than the latter. Sodium, acid, and titanium phosphates, and slag were slightly less favorable than ferric and aluminum phosphate.

DISCUSSION.

The availability of a phosphate will vary with the type of soil, the climatic conditions, and the character of the crop to which it is applied. In view of this, due consideration must be given to the fact that the preceding data have been obtained with only three types of soils and a limited number of crops grown under modified conditions.

The type of Hawaiian soil on which phosphate fertilization is most effective is that known as the red ferruginous clay. According to Hilgard,[1] it would be expected that when water-soluble phosphates are applied to this type of soil, the phosphoric acid would be withdrawn from useful action. Hence any excess that the plant is not able to immediately utilize becomes inert and useless, that is, it combines with the oxids and hydroxids of the trivalent metals, iron and aluminum, and in this form it is for all practical purposes insoluble and inaccessible to the crop. For this reason he advised the use of difficultly-soluble phosphates, such as bone meal and basic slag, which react less readily with iron and aluminum. Until very recent years this has been the generally accepted theory among soil chemists.

The results of more recent investigations, however, indicate that iron and aluminum phosphates are readily available to plants, in many cases more so than the insoluble forms of calcium phosphate, such as bone meal, slags, and floats. Recent work at the Wisconsin Experiment Station,[2] for example, has shown that 9 out of 10 plants tested made better growth when fertilized with aluminum phosphate than with calcium phosphate, while 6 of the 10 made better growth with ferric phosphate.

In view, therefore, of the uncertainty on the subject, the peculiar character of Hawaiian soils, and the practical importance of the matter, it was deemed necessary to study carefully the behavior of various phosphates on typical Hawaiian soils.

The phosphates used as the basis of the preceding experiment are all of commercial importance. Other phosphates were added to the series in order to obtain information relative to the availability of

[1] Soils. New York and London, 1906, p. 357.

[2] Wisconsin Sta. Bul. 240 (1914), p. 22.

the former. Basic slag meal is a waste product in the manufacture of steel, and in addition to 15-20 per cent phosphoric acid, also contains about 30 per cent lime. It has thus far found little application as a fertilizer in Hawaii. Acid phosphate and double superphosphate are manufactured from phosphate rock. The acid phosphate is the simpler product and contains about 20 per cent phosphoric acid as monocalcium phosphate. The double superphosphate, through a modification in the process of manufacture, contains about 45 per cent phosphoric acid as monocalcium phosphate. This class of phosphate fertilizers, more especially the former, is widely used in Hawaii. It may be used with advantage on practically all types of soil which show a deficiency of phosphoric acid. Phosphate rock, known as floats when finely ground, is the natural tricalcium phosphate found in large deposits in various parts of the world, but it is little used in Hawaii. Bone meal is quite widely used as a source of phosphoric acid in Hawaii, but is effective only where the soil receives plenty of water. It is especially effective if applied in connection with green manure. Reverted phosphate, which is primarily dicalcium phosphate, is being used to an increasing extent in the islands. It is prepared by adding lime to acid phosphate.

The results of the experiments indicate that the soluble phosphates are the most effective on Hawaiian soils, especially those of the red-clay type. As already indicated, this is contrary to the conclusions reached by others in regard to the application of soluble phosphates to soils high in iron and aluminum oxids.

Iron and aluminum phosphates are readily available sources of phosphoric acid in Hawaiian soils, the former more so in the first crop in the absence of added lime. In sand cultures the trivalent phosphates surpass the calcium phosphates. Hence, since the precipitated phosphates of iron, aluminum, and even titanium are available to plants, factors other than chemical combination must be considered in order to explain the apparent insolubility of phosphoric acid in Hawaiian soils.

That the phosphoric acid of the red-clay soils of Hawaii exists in some form extremely unavailable to plants is proved by the data obtained in Experiments I and II (pp. 10, 15). The soluble phosphates were the most effective on the first crop. Their effectiveness decreased somewhat in the following crops. The phosphate rock was least effective at the outset, and its effectiveness increased and then decreased as compared with other phosphates, if the weight of succeeding crops may be used as a criterion. Through fermentation changes and chemical action the availability of the phosphate rock was increased to such an extent that the plants of the second millet crop to which this fertilizer was applied had a larger reserve

to draw from and made a better growth than those fertilized with soluble phosphates. The most convincing proof of this statement is furnished by comparing the results of $P_{1/2}$ with those of P_1, $P_{1\ 1/2}$, and P_2. In the second millet crop $P_{1/2}$ phosphate rock gave the best growth, $P_{1/2}$ soluble phosphate being comparatively more exhausted. By comparing $P_{1\ 1/2}$ soluble phosphate with P_2 phosphate rock the former is found to have been considerably more effective. Addition of nitrogen and potash fertilizer failed to prevent the decrease in plant growth due to removal of available phosphates, but upon a further addition of phosphoric acid a marked stimulation resulted.

It has been claimed that lime has a depressing effect upon the assimilation of phosphoric acid from phosphate rock. The results obtained in sand culture did not support this view. It is possible that the apparent depressing effect of phosphate rock in the red-clay soil is due primarily to the conditions in the soil unfavorable to the assimilation of the insoluble phosphates. This kind of phosphate fertilizer is rendered soluble and available as plant food mainly by the action of carbon dioxid and organic acids produced by the micro-organisms of the soil. Aeration in this soil is very low and carbon dioxid is present in almost negligible quantities. Hence if the amount of carbon dioxid present is a measure of bacterial activity, which is known to vary widely in soils according to physical and chemical conditions, then the primary agent upon which phosphate rock depends for its availability is lacking. A further factor may be found in the fact that the acidity of this type is not due to the presence of organic acids, but to conditions the nature of which is yet to be determined.

The table shows the marked increase in assimilation of phosphate rock in the green-manured pots as compared with those unmanured, indicating that the fermentation of green manure and loosening of the soil assisted the millet in assimilating the phosphate rock. The same factors influence the availability of bone meal, which is greater in humic soils where acid-forming bacteria are present.

The amount of phosphoric acid present in each pot, according to the absolute analysis of the soil, was approximately 18.0 grams, while that added as fertilizer ranged from 0.19 gram ($P_{1/2}$) to 0.76 gram (P_2). The analyses of the plants show that the total amount of phosphoric acid removed by the two crops of millet and one of buckwheat, in most instances is equal to that added at the rate of $P_{1/2}$, in several instances to that at the rate of P_2, and in one case to that at the rate of $P_{1\ 1/2}$. The third crop, which was not analyzed, was the most stunted in growth of all the series, indicating, as the analyses show, that the major part of the available phosphoric acid had been removed by preceding crops, leaving only that naturally occurring in the soil. It is plainly evident that the millet was unable to

utilize this phosphate, although it was present in amounts 23 times the largest application and 90 times the smallest. The plants were low and the heads very small.

In Experiment II, in which another application of phosphate was made after harvesting the second crop, the results indicated that the effectiveness was to a slight extent proportional to the amount of phosphate added. The lowest yield was from the $P_{1/2}$ pots, while the highest was from the $P_{1\ 1/2}$ pots. The results as a whole prove the unavailable condition of the phosphate naturally occurring in the red-clay soil, and show further that the addition of any type of phosphate to the soil either assists in the assimilation of that already present, or itself acts as a source of phosphate to the plants.

The fate of soluble phosphates when added to the red-clay soils and their influences upon the physical condition have been quite thoroughly dealt with in previous bulletins of this station.[1] The fixing power of this soil for phosphoric acid has been shown to be so very high and rapid that a loss of phosphate by drainage, through over-application, is impossible. The fixation of the calcium phosphate is greater and more rapid than that of the sodium phosphate, but the sodium of the latter acts as a strong deflocculating agent and would be more completely distributed throughout the soil. This probably explains its greater effectiveness as compared with acid phosphate, which tends to flocculate the soil particles.

Lime was added throughout the experiments on the assumption that it would cause a reversion of the soluble phosphate and thus delay its ultimate combination with the trivalent oxids. From the results obtained, the conclusion is obvious that a normal application of lime is not capable of holding the phosphate in reserve in a form available for the plant and, furthermore, that the benefit derived from the application of the lime, while it may be due in part to its chemical activities, is primarily physical. The action is only temporary, and its influence is exerted to the greatest extent in the first crop. The nature of its action is a flocculation of the clay particles which temporarily disturb the colloidal condition in which the iron and aluminum oxids and hydroxids exist. These compounds, together with some silica, combine to form the clay present in this type of soil. The most important function of this flocculation is to hinder or perhaps only delay the occlusion of the phosphoric acid by the colloids. That the soil does finally return to such a state in due time following the application of lime is indicated by the physical condition of the soil in the pots after the third crop of millet in Experiment II, and the further fact that it had reached a state of apparent acidity, as determined with litmus paper. At the same

[1] Hawaii Sta. Buls. 35 (1914) and 40 (1915).

time there was a decrease in availability of phosphate as measured by the growth of millet.

In the types of Hawaiian soils that contain abnormally high percentages of lime, the phosphate is always present in an available form. This indicates that the lime, when present in such large quantities, is able to perform its function in spite of the excessive quantities of iron and aluminum, but in order that it may exercise this function, it must be present in amounts far in excess of that indicated by the determination of the lime requirement.

The conclusion is evident that the unavailability of the phosphates in the clay soils of Hawaii is not due entirely to their chemical combination with iron and aluminum as phosphates but to other causes of a far more complex nature. The experiments reported in this bulletin, as well as those of several other investigators, have shown the power of certain plants to assimilate the precipitated phosphates of iron and aluminum both when applied in sand cultures and when applied to soils. On the other hand, it will be shown later in this bulletin that the major part of the phosphates of Hawaiian soils does exist in the form of iron and aluminum phosphates and that the addition of soluble phosphates results in a rapid combination with these elements. The answer to the question why plants can not assimilate the phosphates of Hawaiian soils is probably to be found in the realm of soil physics as indicated above.

SUMMARY.

(1) Hawaiian soils are uniformly higher in phosphate than mainland soils, but this is less available, especially in the heavy clay types.

(2) The unavailability of the phosphoric acid in the ferruginous-clay soils is not due entirely to chemical combination but partly to physical occlusion.

(3) Phosphoric acid should be applied to this type of soil in the form of soluble phosphates and in light applications at frequent intervals if rapid returns are anticipated.

(4) In most locations it is poor economy to add bone meal or other difficultly soluble phosphates to Hawaiian soils because they already contain enough insoluble phosphate to grow crops for an indefinite number of years provided the plants had the power to assimilate it.

(5) In wet districts (uplands) phosphate rock, bone meal, basic slag, or reverted phosphate should be very effective, more especially so if applied to highly organic soils or used in systems of diversified agriculture where they may be incorporated with green manure crops.

(6) The availability of all the phosphate fertilizers varies with the fineness, and for this reason all the samples used in the preceding

experiments were ground to as nearly the same degree of fineness as possible. This applies more especially to the insoluble phosphates.

(7) Basic slag is more effective as a source of phosphoric acid than phosphate rock, bone meal, or reverted phosphate.

(8) In field conditions there is not such an abundant supply of water as was used in the pots, hence the soluble phosphates should be relatively more effective under field trials.

(9) Lime applied with phosphates temporarily assists the plants in assimilating phosphoric acid, but it soon loses its effectiveness unless present in excessive amounts.

SOLUBILITY OF DIFFERENT PHOSPHATES IN HAWAIIAN SOILS.

The chemical analyses of Hawaiian soils by solution in hydrochloric acid of specific gravity 1.115 or by fusion with sodium carbonate, with scarcely a single exception, show a far greater amount of phosphoric acid in the soil than would be required for plant growth.

Hawaiian soils are largely a product of the disintegration of basaltic lava and contain abnormally high percentages of iron and aluminum. Likewise, they contain high percentages of phosphoric acid, but in spite of this fact, plants suffer from the lack of phosphoric acid, especially in the red-clay type of soil.

In the work herewith presented, fifth-normal nitric acid, 1 per cent citric acid, 1 per cent sodium hydroxid, hydrochloric acid (specific gravity 1.115), water, and finally fusion with sodium carbonate were used in determining the solubility and combinations of the phosphates. While the voluminous literature regarding the action of these reagents as means of determining the availability of phosphoric acid is very contradictory, in general it may be said that fifth-normal nitric acid acts primarily as a solvent for calcium phosphate, while 1 per cent sodium hydroxid dissolves the iron and aluminum phosphates.

In the experiments here reported, the soils were treated with the solvents as follows: Digested with hydrochloric acid (specific gravity 1.115) according to the official method; digested with 1 per cent citric acid for 3 days with occasional shaking, the proportion of soil to acid being 1 to 10; digested with fifth-normal nitric acid for 5 hours at 40° C. in the same proportion; digested with 1 per cent sodium hydroxid for 5 hours in boiling water in the same proportion, and finally digested with water for 1 week with frequent shaking.

SOLUBILITY OF PHOSPHORIC ACID IN POTTED SOIL.

Following the removal of the first crop of millet on the red-clay soil (Experiment I), samples of soil were taken from all of the pots for analysis. Distilled water, 1 per cent citric acid, and fifth-normal

nitric acid were used as solvents. One hundred grams of soil was shaken with 500 cubic centimeters of water for 1 week and 250 cubic centimeters used for analysis by the colorimetric method. Fifty grams of soil was shaken with 500 cubic centimeters of 1 per cent citric acid, and 20 grams of soil was digested and shaken with 200 cubic centimeters of fifth-normal nitric acid at 40° C. for 5 hours. An analysis was made of 100 cubic centimeters of the nitric acid extract, from which no precipitate could be obtained with molybdate solution. Only a trace of phosphate could be detected by colorimetric determination in 50 cubic centimeters of this solution. The results obtained with water and citric acid are given in Table VIII.

TABLE VIII.—*Solubility of phosphoric acid in the soils in pots of Experiment I.*

Pot Nos.	Fertilizer added.	Soluble in water.	Soluble in citric acid.
		Parts per million.	*Per cent.*
1, 2	N-K-Ca-L	4.8	0.00280
5, 6	N-K-Ca	4.8	.00310
9, 10	N-K-Ca-L	4.4	.00335
13, 14	N-K-Ca	8.0	.00350
17, 18	N-K-Ca-L-$P_{1/2}$ (slag A)	3.8	.00444
21, 22	N-K-Ca-$P_{1/2}$ (slag A)	9.4	.00508
25, 26	N-K-Ca-L-$P_{1/2}$ (slag B)	7.4	.00584
29, 30	N-K-Ca-$P_{1/2}$ (slag B)	5.4	.00537
33, 34	N-K-Ca-L-$P_{1/2}$ (slag C)	4.6	.00537
37, 38	N-K-Ca-$P_{1/2}$ (slag C)	3.0	.00814
41, 42	N-K-Ca-L-$P_{1/2}$ (slag D)	3.0	.00663
45, 46	N-K-Ca-$P_{1/2}$ (slag D)	6.4	.00612
49, 50	N-K-Ca-L-$P_{1/2}$ (acid phosphate)	7.6	.00795
53, 54	N-K-Ca-$P_{1/2}$ (acid phosphate)	4.8	.00558
57, 58	N-K-Ca-L-$P_{1/2}$ (phosphate rock)	6.8	.00493
61, 62	N-K-Ca-$P_{1/2}$ (phosphate rock)	4.8	.00698
65, 66	N-K-Ca-L-$P_{1/2}$ (sodium phosphate)	5.2	.00652
69, 70	N-K-Ca-$P_{1/2}$ (sodium phosphate)	6.0	.00730
73, 74	N-K-Ca-L-P_1 (slag A)	6.0	.00809
77, 78	N-K-Ca-P_1 (slag A)	4.0	.00665
81, 82	N-K-Ca-L-P_1 (slag B	3.4	.00557
85, 86	N-K-Ca-P_1 (slag B)	3.4	.00649
89, 90	N-K-Ca-L-P_1 (slag C)	3.4	.00493
93, 94	N-K-Ca-P_1 (slag C)	2.6	.00728
97, 98	N-K-Ca-L-P_1 (slag D)	2.8	.00255
99, 102	N-K-Ca-P_1 (slag D)	3.0	.00270
105, 106	N-K-Ca-L-P_1 (acid phosphate)	3.4	.00255
109, 110	N-K-Ca-P_1 (acid phosphate)	3.2	.00303
113, 114	N-K-Ca-L-P_1 (phosphate rock)	2.2	.00222
117, 118	N-K-Ca-P_1 (phosphate rock)	2.6	.00255
121, 122	N-K-Ca-L-P_1 (sodium phosphate)	2.8	.00715
125, 126	N-K-Ca-P_1 (sodium phosphate)	2.8	.00525
129, 130	N-K-Ca_x-L-P_1 (sodium phosphate)	4.0	.00780
133, 134	N-K-Ca_x-P_1 (sodium phosphate)	3.2	.00413
137, 138	N_1 1/2-K_1 1/2-Ca-L-P_1 (sodium phosphate)	5.4	.00255
141, 142	N_1 1/2-K_1 1/2-Ca-P_1 (sodium phosphate)	3.2	.00431
145, 146	N-K-Ca-L-P_1 1/2 (sodium phosphate)	2.4	.01275
149, 150	N-K-Ca-P_1 1/2 (sodium phosphate)	3.2	.00828
153, 154	N-K-Ca-L-P_2 (phosphate rock)	2.4	.00619
157, 158	N-K-Ca-P_2 (phosphate rock)	4.8	.00716
161, 162	N-K-Ca-L-$P_{1/2}$ (superphosphate)	2.6	.00619
165, 166	N-K-Ca-$P_{1/2}$ (superphosphate)	2.6	.00652
169, 170	N-K-Ca-L-P_1 (superphosphate)	6.8	.00731
173, 174	N-K-Ca-P_1 (superphosphate)	5.8	.00717

Owing to the high fixing power of this type of soil, the analysis of the water extracts would not be expected to show any great variation in solubility. Such proved to be the case, and it is probable

that precipitation or fixation from the extract may have taken place, since the process of extraction was extended over a period of one week. The results as a whole indicate the impossibility of determining any increase in concentration of the soil solution in this type of soil as regards phosphoric acid by means of extraction with distilled water.

The results from treatment with citric acid were somewhat different. Practically all pots to which phosphates were added showed a greater solubility in this solvent than the check pots. Furthermore, the solubility was more or less dependent upon the amount of phosphate added to the pots. The pots showing the largest amount of phosphate soluble in citric acid were those to which sodium phosphate had been added at the rate of 0.021 per cent, and these pots also produced the best growth.

It is evident from the results obtained by extraction with fifth-normal nitric acid that, if this acid is a solvent for calcium phosphate, the lime added had little influence as regards combination with the phosphate, since the acid extracted little more than a trace of phosphate from the soil.

SOLUBILITY OF PHOSPHATE FERTILIZER AFTER ADDITION TO THE SOIL.

While the preceding data indicated a variation in the solubility of different types of phosphate, in order to study the relation more thoroughly a series of experiments was planned, using the red-clay soil. Nineteen portions of soil of 100 grams each were weighed into large porcelain dishes. Duplicate portions of this soil were treated with each of the following phosphates, added at the rate of 1 per cent P_2O_5: Acid phosphate, superphosphate, slag, phosphate rock, tripotassium phosphate, monosodium phosphate, disodium phosphate, commercial sodium phosphate, and monocalcium phosphate. The remaining portion was used as a check. After the addition of the phosphate the soil was well mixed and saturated with water, then exposed to air and sunlight to dry and weather. Saturation and drying was repeated twice. Upon the third drying, after about two months' time, the different portions of soil were transferred to percolators, and 700 cubic centimeters of distilled water was allowed to percolate through each sample. A separate analysis was made of each 100 cubic centimeters of the percolate. The results are given in Table IX.

TABLE IX.—*Phosphoric acid soluble in water.*

[Expressed in parts per million.]

Phosphate added.	Percolates of 100 cc. each.						
	First 100.	Second and third 100.	Fourth 100.	Fifth 100.	Sixth 100.	Seventh 100.	Total.
Acid phosphate	26	16	26	38	11	21	138
Do	28	20	26	27	29	16	146
Superphosphate	36	70	60	58	46	16	286
Do	36	66	60	58	48	21	289
Slag	Trace.	4	6	6	6	9	31
Do	Trace.	4	4	10	.....	6	24
Phosphate rock	4	4	4	4	4	4	24
Do	4	4	4	4	4	4	24
Commercial sodium phosphate	Trace.	Trace.	.....	.....	.....	.....	.....
Do	Trace.	4	25	14	22	17	82
Disodium phosphate	Trace.	4	25	16	28	7	80
Do	Trace.	4	28	10	22	11	75
Monosodium phosphate	Trace.	38	40	4	30	18	130
Do	Trace.	66	60	48	29	24	227
Tripotassium phosphate	Trace.	4	14	15	12	9	54
Do	Trace.	4	16	8	16	17	61
Monocalcium phosphate	62	.....	70	76	82	21	311
Do	54	100	95	70	76	33	428
Check	3	4	4	4	.....	.....	.....

After 700 cubic centimeters had passed through, the soil was removed from the percolators and extracted with 1 per cent citric acid according to the Dyer method. The solubility in this solvent is given in Table X.

TABLE X.—*Phosphoric acid soluble in 1 per cent citric acid.*

[Expressed in per cent of air-dry soil.]

Phosphate added.	Per cent.	Phosphate added.	Per cent.
Acid phosphate	0.210	Commercial sodium phosphate	0.180
Do	.204	Disodium phosphate	.154
Superphosphate	.182	Monosodium phosphate	.242
Do	.192	Do	.198
Slag	.138	Tripotassium phosphate	.124
Do	.151	Do	.122
Phosphate rock	.204	Monocalcium phosphate	.222
Do	.202	Do	.222
Commercial sodium phosphate	.212	Check	.019

The results clearly show the rapid fixation which takes place when soluble phosphates are added to the soil as well as the solubility of the phosphates after fixation.

In view of these results, a further set of experiments was planned in order to study the comparative action of iron and aluminum phosphates. If soluble phosphates revert to iron and aluminum phosphates, it is desirable to study the solubility of the latter. This series was carried out in the same manner as the previous one except that separate samples were extracted and a larger quantity of soil—that

is, 25 grams of soil to 250 cubic centimeters of solvent—was used. Additional solvents were used in order to make the experiment complete. The results are given in Table XI.

TABLE XI.—*Solubility of phosphoric acid, added at the rate of 1 per cent, in red-clay soil.*

Fertilizer added.	Soluble in water.	Soluble in fifth-normal nitric acid.	Soluble in 1 per cent citric acid.	Soluble in 1 per cent sodium hydroxid.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
Acid phosphate	0.0099	0.297	0.237	0.222
Phosphate rock	.0027	.251	.181	.077
Sodium phosphate	.0848	.353	.304	.632
Tripotassium phosphate	.0249	.217	.152	.442
Ferrous phosphate	Trace.	.496	.385	.720
Do	Trace.	.464	.380	.528
Ferric phosphate	Trace.	.346	.235	.494
Do	Trace.	.319	.208	.360
Check	Trace.	Trace.	.0025	.052

These results indicate that a large part of the soluble phosphates does revert to the iron and aluminum phosphates.

SOLUBILITY OF PHOSPHATE NATURALLY OCCURRING IN HAWAIIAN SOILS.

Table XII, showing the relatively small quantities of phosphoric acid dissolved out of Hawaiian soils by fifth-normal nitric acid, which is a solvent of calcium phosphate, and the larger quantities soluble in 1 per cent sodium hydroxid, which is a solvent of iron and aluminum phosphates, indicates that the major part of the phosphates in these soils exists normally in combination with iron and aluminum.

TABLE XII.—*Solubility of phosphoric acid in various types of Hawaiian soils.*

[Expressed as per cent P_2O_5.]

	Soil No. 1.	Soil No. 2.	Soil No. 3.	Soil No. 4.	Soil No. 5.	Soil No. 6.	Soil No. 7.	Soil No. 8.	Soil No. 9.	Soil No. 10.	Soil No. 11.
Hydrochloric acid (specific gravity 1.115)	0.677	0.28	0.289	2.171	0.427	0.286	0.116	0.104	0.024	0.234	0.225
One per cent citric acid	.152	.0036	.0033	.324	.008	.005	.004	.003	.....	.....	.004
Fifth-normal nitric acid	.007	.0024	.0018	.015	.0005	.0003	.0004	.0003	.0001	.0013	.0005
One per cent sodium hydroxid	.153	.0363	.0615	.222	.298	.279	.052	.055	.008	.008	.043
Total phosphoric acid as determined by fusion with sodium carbonate	1.060	.670	.710	3.300	.440	.460	.240	.450	.030	.400	.340
Phosphoric acid in humus, per cent	22.98	1.09	1.02	4.96	2.98	2.38	1.23	1.36	0.530	1.110	0.930
Humus in soil.....per cent	1.49	3.48	4.93	7.96	3.83	3.93	3.50	3.78	1.690	1.630	6.960

In selecting the soils to be tested, several widely varying types were chosen. No. 1 is a sandy soil high in magnesia (8.74 per cent) and lime (1.84 per cent) and is the same as No. 1 in the pot experiments, which did not respond to phosphate fertilizers; Nos. 2 and 3 are the

same as in the pot experiments; No. 4 is a very productive silt, high in lime (3.80 per cent) and humus; Nos. 5 and 6 are brown-clay soils belonging to the class of clays which contain a larger amount of iron than aluminum; Nos. 7 and 8 are clay soils belonging to the class of clays which show a higher content of aluminum than iron; No. 9 is a soil containing 20 per cent titanium, about 40 per cent iron oxid, and 8 per cent aluminum; No. 10 is a soil which is principally coral sand (about 90 per cent calcium carbonate); No. 11 is a sandy soil from a humid district and is high in both lime (6.3 per cent) and magnesia (5.8 per cent). These 9 types of soils include all the important ones of the islands, for which reason the data should be of wide application in drawing conclusions regarding the locking up of the phosphate.

The data given in the table show that there are included soils which possess all the conditions generally considered essential for the fixation of phosphates. There are the normal conditions, such as high clay content, colloidal clay, and organic compounds, which promote physico-chemical absorption; the humic conditions which promote biological absorption; and, finally, the chemical conditions, such as high content of lime, magnesium, iron, aluminum, and titanium, which, either through an actual combination or a reversion to a less soluble form, influence chemical fixation. At least one or possibly all three of the above factors may influence the maintenance of a favorable medium in the soil for plant growth, in so far as plant growth is affected by the presence of a readily available source of phosphoric acid. A relation may be established from data given in Table XII between the chemical and physical composition of the soil, the solubility of phosphoric acid in various solvents, and its availability as measured by plant growth.

Table XII shows the relative solubility of phosphoric acid in all the important soil types of the Hawaiian Islands. Since three of these types, Nos. 1, 2, and 3, were used in the pot experiments, a comparison of the data will indicate the relation between the solubility and the availability as measured by the growth of millet. Soil No. 1 did not respond to phosphate fertilizer, thus showing the high availability of its phosphoric acid; soil No. 2 was greatly in need of available phosphates, as indicated by the marked increase in plant growth following the application of phosphate fertilizers in all forms; soil No. 3 was less in need of phosphate than No. 2, as indicated by a smaller increase resulting from the addition of phosphate. The other soils have not been used in pot experiments. The results of previous experiments [1] with soils of the same type as certain of those included in Table XII are summarized in Table XIII.

[1] W. P. Kelley, Jour. Indus. and Engin. Chem., 2 (1910), p. 277.

TABLE XIII.—*Solubility and availability of phosphoric acid in ferruginous soils.*

Soil No.	Soluble in fifth-normal hydrochloric acid.	Soluble in 1 per cent sodium hydroxid.	Crop grown.	Crop increase from phosphate.
	Per cent.	*Per cent.*		*Per cent.*
10	Trace.	0.0060	Pineapples	50
11	Trace.	.0219	do	100
12	Trace.	.0089	Cotton	200
13	0.1128	.1858	Rice	No effect.

Soils Nos. 10, 11, and 12 are samples of red soil of the type used in the pot experiments, responding to phosphate fertilization, while No. 13 is a sample of the same soil used as No. 1 in the pot experiments. Hence it may be seen that the results are directly in accord with those presented in this bulletin.

Table XII shows clearly the insoluble nature of the phosphoric acid in the different types of soil. Fusion with sodium carbonate shows the total phosphate content to be very high in practically all types. The results of the official method of extraction with hydrochloric acid (specific gravity 1.115) throw considerable discredit upon its usefulness as a means of determining the phosphate content of Hawaiian soils. This may be attributed to several causes, chief among which is the inability of the acid to penetrate to such an extent during the period of extraction as to come in contact with any occluded crystals or other protected particles of phosphate, and, furthermore, its lack of ability thoroughly to decompose the basic phosphates of iron, aluminum, and titanium, especially the last. The obvious conclusion to be drawn from these results is the uselessness of determining the phosphoric acid in the hydrochloric acid extract and the need of determining the absolute phosphate content.

The action of weak solvents upon the various types of Hawaiian soils is a means of obtaining data of value regarding the solubility of phosphoric acid, but not regarding its availability. Neither is it possible to determine in this way whether the soil will respond to phosphate fertilization. Stoddard[1] says that, for Wisconsin at least, if a soil contains less than 0.015 per cent of phosphoric acid soluble in fifth-normal nitric acid, it will respond to phosphate fertilization. Snyder,[2] working independently, reached the same conclusion in regard to Minnesota soils. That such a relation holds good for Hawaiian soils does not at this time appear probable, primarily because there are too many other abnormal factors to be considered. Soil No. 1 has been shown not to respond measurably to phosphate applications, yet it contains only 0.007 per cent phosphoric acid soluble in fifth-normal nitric acid, but, on the other hand, contains

[1] Wisconsin Sta. Research Bul. 2 (1909). [2] Minnesota Sta. Bul. 102 (1907), p. 36.

0.153 per cent soluble iron and aluminum phosphates. The weak solvents apparently exert a very limited solvent action, as is shown by the small percentage of the total phosphoric acid dissolved. All the soils, irrespective of type, contain iron and aluminum phosphates far in excess of calcium phosphates. Citric acid is a much more effective solvent than nitric acid.

The humus content of Hawaiian soils varies between wide limits according to locality and climatic conditions. Since humus is a factor in the availability of phosphoric acid, some determinations were made of the humus content of various types and also of the phosphoric acid combined with the humus. There is apparently no relation between the amount of humus in the soil and the phosphate content of the humus. Stoddard [1] found that as the amount of humus decreases the percentage of phosphoric acid in the humus increases. This is not true of Hawaiian soils, but, as a general rule, it may be said that those high in lime or magnesia and humus contain a large percentage of phosphoric acid organically combined. Attention is called to the high phosphate content of soil No. 1, in which the humus contains 22.98 per cent phosphoric acid. In view of the fact that this soil has been found not to respond to phosphate fertilization and yet to have a very low content of calcium phosphate, as measured by fifth-normal nitric acid, the conclusion is evident that the organic phosphate in this soil is present in a readily available form.

The soils having the strongest fixing power are likewise those containing phosphoric acid in least available form as measured by plant growth and also those containing the least phosphoric acid soluble in weak solvents. These phosphates are only slightly soluble in citric and nitric acids, but are more soluble in weak alkali. The soils of lowest fixing power, due primarily to lower clay content, are high in lime and magnesia. These soils are also high in phosphate, and while a large percentage is in the form of iron and aluminum phosphate, the proportion soluble in citric acid is equal to or more than that soluble in alkali. An exception to this, and one to which attention should be called, is soil No. 11. This soil is high in lime, magnesia, and humus, but was taken from a very humid district. The analysis shows the major part of the calcium phosphate to have been washed out, leaving the iron and aluminum phosphates. This is probably similar to the action of weathering agents upon lava in the original Hawaiian soil formation, as a result of which lime has decreased from about 10 per cent to less than 1 per cent in the average soils. The phosphoric acid has decreased quite often also during this process of disintegration.

Soils Nos. 2, 3, 5, 6, 7, and 8 are all clay soils. Nos. 5, 6, 7, and 8 were chosen for the fact that in the two former the iron content is in

[1] Wisconsin Sta. Research Bul. 2 (1909).

excess of the aluminum, while in the two latter the opposite relation exists. If it is permissible to assume that the phosphate is largely in combination with iron in soils Nos. 5 and 6, while that in Nos. 7 and 8 is largely in combination with aluminum, then the former is more soluble and, as results have shown, slightly more available. On the other hand, Hawaiian clay soils, in which the aluminum content is higher than the iron, possess more marked colloidal properties, and hence, due to their physical influences, should contain phosphoric acid in a less soluble and less available form.

It appears that the solubility of the phosphates already present in the soil is dependent partly upon conditions of equilibrium which influence the concentration of the soil solution. One effect of an added fertilizer is to disturb this state of equilibrium. For this reason the solubility or availability of an added phosphate will depend upon its action following its addition to the soil, and hence is influenced by several factors.

Reference to Tables IX, X, and XI will clearly show that the solubility of the phosphates before adding to the soil can not be used as a criterion of their solubility after addition. According to the results tabulated in Table IX, fixation is apparently influenced by the valency of the salt. Trivalent potassium phosphate is fixed most strongly, divalent sodium phosphate next strongest, while monovalent sodium phosphate is most soluble. Superphosphate is much more soluble than the sodium and potassium phosphates, as is also acid phosphate, with the exception of monosodium phosphate. These facts indicate that the fixing or reversion of the calcium phosphate is much less rapid than that of the sodium and potassium salts, or possibly that the calcium salt is not so strongly fixed. But this does not correlate with the availability as measured by the plant growth in this soil, where sodium phosphate was the most effective phosphate fertilizer. The sodium and potassium salts were least soluble in the first portion of water passing through the soil, and in this they differed radically from the calcium salts. This indicates the possible influence of physical factors upon their solubility. Phosphate rock and slag proved to be the least soluble in water.

The solubility, as measured by citric acid (Table X), indicates that citric acid only magnifies the action of water. All forms of calcium phosphate were among the most soluble, except Thomas slag (tetracalcium phosphate). The solubility in citric acid is also influenced by the valency of the sodium and potassium phosphate, namely, the monobasic phosphate is most soluble while the tribasic is least soluble.

Somewhat more complete data are given in Table XI. The solubility in water is slightly different from that given in the previous

table, due to a difference in method of extraction. It may be safely said that the method of percolation more nearly represents soil conditions. The motive in using several solvents was to determine the combinations formed in the soil by the phosphates. The data show sodium and potassium phosphates to be readily converted into iron and aluminum phosphates. These salts also show a high solubility in fifth-normal nitric acid, indicating either a residue unconverted as shown in column 3, or a partial conversion to the soluble calcium salt, which would be the only calcium salt possible of formation in the absence of an excess of lime. The iron phosphates proved to be quite soluble in fifth-normal nitric acid, in fact, to a greater degree than the calcium salts, acid phosphate, and phosphate rock. Tripotassium phosphate is, in all solvents, less soluble than disodium phosphate.

It may be said, then, that soluble phosphates, when added to Hawaiian soils, combine with iron and aluminum to a greater degree than with calcium, even in soils containing a high percentage of the last. But this chemical combination in itself does not explain the unavailable nature of phosphates in the soils, as is shown in the results obtained from both the pot experiments and the solubility experiments noted in the latter half of this bulletin. The unavailable condition is brought about through physico-chemical activities, and is more rapid when a sodium or potassium phosphate is added, because of the rapid deflocculation of the clay, which causes more complete dissemination of the salts.

As a means of measuring solubility, all solvents used are of more or less value. Solubility can hardly be considered a measure of availability except in so far as a comparison of the solubility in several of the solvents will indicate the form in which the phosphoric acid is combined in the soil. As the above data show, the results obtained by the use of the different solvents are quite conflicting on certain soils.

At the beginning of this work the most plausible theory suggested to explain the unavailability of the phosphoric acid in Hawaiian soils seemed to be its possible combination with titanium. While it is undoubtedly true that the phosphoric acid may be present to a certain extent in this form, which is highly insoluble, this fact is of minor importance in explaining the low availability, although it is perhaps the most serious chemical factor. Titanium is widely distributed in Hawaiian soils, which contain, on the average, from 5 to 10 per cent of titanium oxid, and as much as 34 per cent has been found. If this constituent were to be considered a prime factor in the availability of the phosphoric acid, it would be expected that the titanium soils would have a high phosphate content, due to retention of the phosphoric acid as titanium phosphate. The analysis of

this type of soil, as shown in Table XIV, can hardly be said to support this theory.

TABLE XIV.—*Partial analysis of titanium soils.*

Soil No.	Titanium oxid (TiO_2).	Phosphoric acid soluble in hydrochloric acid.	Total phosphoric acid.	Soil No.	Titanium oxid (TiO_2).	Phosphoric acid soluble in hydrochloric acid.	Total phosphoric acid.
	Per cent.	*Per cent.*	*Per cent.*		*Per cent.*	*Per cent.*	*Per cent.*
33	21.90	0.04	0.22	165	20.62	0.04	0.17
72	28.64	.05	.56	174	18.84	.11	.50
113	27.49	.09	.34	175	20.02	.11	.27
164	18.90	.07	.08	199	34.16	.04	.35

Titanium and total phosphoric acid were determined by fusion with sodium carbonate.

The above figures indicate the insolubility of titanium phosphate, but also show the low phosphate content of this type of soil. The average phosphate content of Hawaiian soils is about 0.5 per cent P_2O_5, while the maximum is 2.32 per cent (determined with hydrochloric acid of specific gravity 1.115), and the maximum absolute phosphate content as determined by fusion with sodium carbonate is 3.50 per cent. It appears, therefore, that the major part of the phosphoric acid combined with the titanium in the lava rock remains as such in the soil and represents the chemically combined insoluble phosphate, but owing to the inert properties of the titanium as compared with the other elements present in the soil, it may be considered to be inactive toward other phosphates already present or any which may be added as fertilizers.

SUMMARY.

(1) Hydrochloric acid of official strength does not dissolve all of the phosphoric acid of Hawaiian soils. To determine the total phosphate content, it is necessary to fuse the soil with sodium carbonate.

(2) Fifth-normal nitric acid has very little solvent action upon the phosphate in the soils, indicating the absence of appreciable quantities of calcium phosphate.

(3) One per cent citric acid has a much stronger solvent action than fifth-normal nitric acid.

(4) Of the weaker solvents, 1 per cent sodium hydroxid is the strongest, due to its action on the iron and aluminum phosphates.

(5) The fertilizer (phosphate) requirement of the soil is not measured by solubility in water or fifth-normal nitric acid, but it may be indicated by the solubility in citric acid.

(6) The solubility of a phosphate before it is added to a soil can not be used as a criterion of its solubility after addition, but it may indicate its availability.

(7) The fixation of a soluble phosphate by the soil may be influenced by the basicity of the soil.

(8) Availability as determined with solvents does not agree in full with that indicated by plant growth.

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APPENDIX.

THE DETERMINATION OF PHOSPHORIC ACID IN HAWAIIAN SOILS.

During the course of a great many soil analyses in this laboratory, it has been found that influences of an inhibitory nature seriously affect the determination of phosphoric acid in the hydrochloric acid extract of Hawaiian soils. The error resulting has always been attributed to the presence of titanium, although no work has been done to establish this theory definitely.

The nature of the error is indicated by the appearance of a white precipitate upon dissolving the yellow phosphomolybdate precipitate in ammonia. A part of this white precipitate may pass through the filter paper and appear in the filtrate in a flocculent form which settles out on standing overnight, or it may be precipitated before passing through the filter paper and hence mask the appearance of the error. In many soil extracts it is present in appreciable amounts, producing seriously misleading results. On dissolving the yellow precipitate on the paper by treating first with hot water and then making alkaline on the filter with ammonia, a larger precipitate is obtained than if it were dissolved by a hot solution of ammonia.

The size of the error due to this white precipitate is indicated by the data in Table XV showing the difference in phosphate content of f12 Hawaiian soils as determined by the official method. In one series the precipitate was removed before adding the magnesia mixture, in another the magnesia mixture was added directly.

TABLE XV.—*Variation in phosphoric acid content as determined by different methods.*

Method.	Soil No. 1.	Soil No. 2.	Soil No. 3.	Soil No. 4.	Soil No. 5.	Soil No. 6.	Soil No. 7.	Soil No. 8.	Soil No. 9.	Soil No. 10.	Soil No. 11.	Soil No. 12.
	P. c.	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*
Filtered	0.299	0.311	0.346	0.304	0.412	0.330	0.280	0.526	0.515	0.277	0.302	0.445
Not filtered	.395	.399	.419	.349	.596	.495	.446	.733	.824	.445	.402	.607
Volumetric	.175	.188	.224	.227	.204	.....	.....	.569	.514	.219	.240	.382

As indicated in the table, the error varies from 0.073 per cent to 0.309 per cent, depending on whether the white precipitate is removed by filtration or weighed as magnesium pyrophosphate. The volumetric method of titrating the yellow phosphomolybdate with standard alkali does not eliminate the error, but for comparison, the determination by this method is given in the table.

Among the elements which must be considered as having the greatest influence upon the determination of phosphoric acid in soils are iron, aluminum, titanium, and silicon. Hence, in choosing soils for use in the present investigation, only those showing certain peculiarities were selected. Partial analyses of the soils are given in Table XVI.

TABLE XVI.—*Partial analysis of soils by hydrochloric acid (specific gravity extraction 1.115).*

	Soil No. 1.	Soil No. 2.	Soil No. 3.	Soil No. 4.	Soil No. 5.	Soil No. 6.	Soil No. 7.	Soil No. 8.	Soil No. 9.	Soil No. 10.	Soil No. 11.	Soil No. 12.
	P. c.	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*
Ferric oxid	14.84	13.28	15.72	11.60	15.16	19.32	25.26	25.28	31.00	25.20	30.56	30.84
Aluminum oxid	18.20	26.25	24.78	26.01	19.55	21.76	7.03	17.43	15.81	19.63	11.94	10.68
Titanium oxid	1.40	1.40	1.80	1.20	2.20	3.00	5.40	5.20	5.00	4.20	5.20	6.20
Insoluble residue	35.21	30.52	29.64	28.57	29.22	30.57	30.54	29.20	28.65	27.03	33.35	34.34

Since the insoluble condition of phosphates in Hawaiian soils is partly due to physical influences, only soils of the red-clay types were used in this work. Soils Nos. 1 to 6, inclusive, represent the type of highly colloidal soil in which the aluminum content is in excess of the iron. In Nos. 7 to 12, inclusive, the opposite relation exists between the iron and aluminum. These relationships influence to a considerable extent both the physical and chemical properties of the soil, and in the latter type, that is, those in which the iron is in excess, the formation of the white precipitate is more prevalent. It should also be mentioned that the latter are also higher in titanium than the former. An analysis of this white precipitate shows it to contain about 25 per cent of titanium oxid, 70 per cent of iron and aluminum oxids, small amounts of phosphoric acid, and no silica. Hence an error will result in the determination whether the precipitate is filtered off or weighed as magnesium pyrophosphate. The only solution of the problem is a prevention of the deposition of the white precipitate or a removal of the inhibiting factors. That titanium and iron, primarily the former, are the elements most active toward its formation may be seen by reference to the table of analyses and to the table showing the weight ot white precipitate deposited. The greatest error occurs in those soils containing the highest percentage of iron and titanium, but the total elimination of these elements in the soil extract without removing traces of phosphate is a practical impossibility.

A method for removing silica and titanium from the soil extract recommended by the Association of Official Agricultural Chemists is to evaporate the extract to dryness and take up in hydrochloric acid. This method fails utterly when applied to local soils and is never used in this laboratory. Instead, all soil analyses are made directly upon

the acid extract after oxidizing the iron and organic matter with nitric acid.

In order to illustrate the loss in phosphoric acid, as well as other elements, resulting through an evaporation of the soil extract to dryness, the following table is inserted. Fifty cubic centimeters of each extract, representing 1 gram of soil, was evaporated to dryness, taken up in hydrochloric acid, filtered, phosphoric acid determined in the filtrate, and the insoluble residue analyzed.

TABLE XVII.—*Composition of insoluble residue formed on evaporating soil extract to dryness.*

	Soil No. 1.	Soil No. 2.	Soil No. 3.	Soil No. 4.	Soil No. 5.	Soil No. 6.	Soil No. 7.	Soil No. 8.	Soil No. 9.	Soil No. 10.	Soil No. 11.	Soil No. 12.
	P. c.	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*	*P. c.*
Total residue	0.27	0.24	0.14	0.12	0.12	0.01	1.55	2.66	2.32	5.50	3.58	3.06
Silica	.23	.22	.14	.12	.12	.01	.00	.00	.00	.08	.00	.22
Titanium oxid	(1)	(1)	(1)	(1)	(1)	(1)	1.05	1.85	1.50	4.30	2.35	2.00
Iron oxid	Tr.	Tr.	Tr.	Tr.	Tr.	Tr.	.18	.22	.18	.33	.18	.18
Phosphoric acid	Tr.	Tr.	Tr.	Tr.	Tr.	Tr.	.10	.67	.20	.15	.12	.08
Aluminum oxid	(1)	(1)	(1)	(1)	(1)	(1)	.32	.59	.64	.71	1.05	.44

[1] Not determined.

While this method does eliminate the formation of the white precipitate and indicates the primary source of error to be titanium, all possibility of its use as a method for determining phosphoric acid in the soil extract is precluded by the results in the above table. Attention is called to the remarkable difference in the properties of the two chemical types.

After a thorough trial of several methods and modifications the elimination of the white precipitate was successfully effected by a precipitation in a nitric-acid solution free from chlorids. The following method has been adopted:

To 50 cubic centimeters of the hydrochloric-acid extract, representing 1 gram of soil, add 1 cubic centimeter of nitric acid and boil to oxidize the organic matter and ferrous iron. Add ammonium hydroxid until faintly alkaline, boil to remove excess of ammonia, filter, and wash free of chlorids. Transfer filter and contents to the original beaker, add an excess of dilute nitric acid, and heat to boiling on the hot plate in a covered beaker. This procedure is necessary to dissolve portions of the ammonia precipitate which assumes a colloidal form on boiling in an ammoniacal solution insoluble in cold nitric acid. In case too large an excess of nitric acid has been added, it should be nearly neutralized with ammonia, several grams of ammonium nitrate added, the solution diluted to 100 to 150 cubic centimeters, and 50 cubic centimeters of molybdate solution added slowly while stirring. The beaker is then placed in a water bath at 55° C. for four hours. Further procedure is the same as that of the official method.[1]

[1] U. S. Dept. Agr., Bur. Chem. Bul. 107 (rev.), 1908.

It was found that by the above procedure the phosphomolybdate is thrown down in four hours' time, leaving a clear supernatant liquid. In cases where it is possible it is best to let the precipitate stand overnight, although in all cases where duplicate determinations were made with some standing overnight and others four hours for the deposition of the yellow precipitate, closely agreeing results were obtained. The addition of excessive amounts of ammonium nitrate to the hydrochloric acid extract does not offset the influence of the chlorids. It was found that the presence of chlorids caused an excessive precipitation of molybdic acid also.

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